length have been observed in the type II reaction of alkyl phenyl ketones.[28,29] This question will be considered in a subsequent communication.[30]

Conclusions

From these experiments it appears that the processes of electronic energy transfer in polymeric ketone systems both in solution and in the amorphous bulk phase above T_g are rather similar to those observed with smaller molecules. The lifetimes of the excited states appear to be of the same order of magnitude and the collisional efficiency for energy exchange nearly identical. Bimolecular processes involving reaction from excited states will be altered in polymer systems primarily by the difference expected in the diffusion rates of interacting species, particularly in the bulk phase.

The utility of energy transfer processes for the stabilization of polymers will depend to a large extent on the lifetime of the excited states involved. In the present instance involving aliphatic carbonyl groups, the excited state lifetimes, τ, are so short that excessive concentrations of the stabilizer molecules would be required to obtain an economically desirable effect. However, other polymers, particularly those containing phenyl groups, might be expected to have longer lifetimes and hence would be easier to stabilize by this mechanism. In view of this, the study of energy transfer processes in other polymers may well lead to important advances in the development of stabilizer systems.

Acknowledgment. The authors wish to acknowledge the financial support of the National Research Council of Canada and a fellowship (M. H.) from the Xerox Corp.

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[28] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5896 (1968).

[29] J. N. Pitts, Jr., D. R. Bowley, J. C. Manis, and A. D. Broadbent, *ibid.*, **90**, 5900 (1968).

[30] M. Heskins and J. E. Guillet, in preparation.

Diffusion-Controlled Oxidative Degradation of Isotactic Polystyrene at Elevated Temperatures.
I. Experimental Procedure and Results

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Received May 1, 1969

ABSTRACT: The thermal-oxidative degradation of isotactic polystyrene has been studied in closed quartz spoon gauge reaction vessels over a temperature range from 249 to 300°. Changes in initial gas pressure, oxygen consumption, hydroperoxide formation, volatile formation, chain scission, and uv spectra were measured as a function of temperature and initial oxygen pressure. Chromatography showed that volatiles consist mainly of water during the initial stage of degradation. The residues of isotactic and atactic polymer, respectively, were also investigated by chromatography after prolonged oxidation. The value for the energy of activation for oxygen consumption and the dependence of the degradation on polymer film thickness indicate that the oxidation process is diffusion controlled.

Aspects of oxidative degradation of polystyrene have been studied repeatedly. Work published before 1955 was reviewed by Jellinek[1] and the relevant literature up to about 1962 was discussed by Tryon and Wall.[2] A review article and a book on oxidative degradation of polyolefins appeared recently by Reich and Stivala.[3] A book by Neiman[4] and a chapter by Jellinek[5] in a recent book on stereospecific polymers are relevant in this connection. Nmr, uv, and ir spectra during oxidative degradation were obtained and discussed by Beachell and Smiley.[6]

A comprehensive investigation of the oxidative degradation of isotactic polystyrene, taking into account a number of relevant parameters of importance for the process, does not appear to have been carried out. Such parameters are, for instance, oxygen consumption, peroxide formation, chain scission, volatile formation, reactions at side groups, change in spectra, etc. In 1949, Jellinek[7] studied the oxidative degradation of atactic polystyrene, but only from the standpoint of chain scission.

It seems to be generally agreed that initiation of the oxidative process in the case of polystyrene is due to abstraction of tertiary hydrogen atoms. The polymer radicals thus formed react with oxygen, forming first hydroperoxide radicals and subsequently hydroperoxide

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[1] H. H. G. Jellinek, "Degradation of Vinyl Polymers," Academic Press, New York, N. Y., 1955.

[2] M. Tryon and L. S. Wall in "Autoxidation and Antioxidants," L. Lundberg, Ed., Interscience Publishers, New York, N. Y., 1962, Chapter 19.

[3] L. Reich and S. S. Stivala, *Rev. Macromol. Chem.*, **1**, 249, (1966). See also L. Reich and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins," Marcel Dekker, Inc., New York, N. Y., 1969.

[4] M. B. Neiman, Ed., "Aging and Stabilization of Polymers," Consultants Bureau, New York, N. Y., 1965.

[5] H. H. G. Jellinek, "The Stereochemistry of Macromolecules," Vol. 3, A. D. Ketley, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, Chapter 10.

[6] H. C. Beachell and L. H. Smiley, *J. Polym. Sci., Part A-1*, **5**, 1635 (1967).

[7] H. H. G. Jellinek, *J. Polym. Sci.*, **4**, 1 (1949).

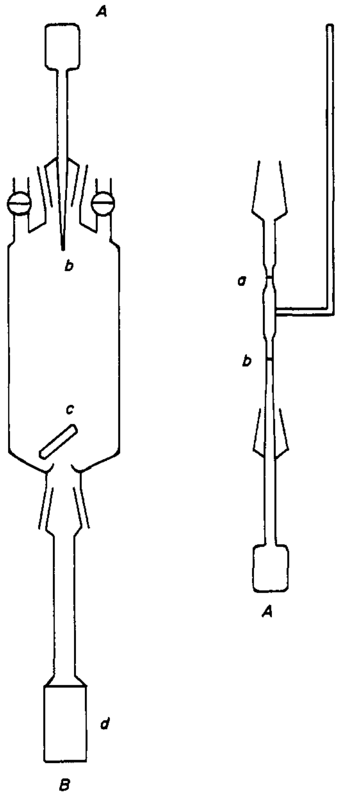

Figure 1. Apparatus for oxygen measurements: A, quartz vessel for the preparation of polymer film and for oxidative degradation, (a) first sealing point after introduction of O_2, (b) second sealing point after degradation (volume a to b is negligible), r quartz rod; B, quartz tubing and 1-cm spectrophotometric cell d; c stirrer and breaking device for vessel A at point b.

groups by further abstraction of tertiary hydrogen atoms from other chain molecules. The hydroperoxide eventually decomposes, leading to volatile products, chain scission and oxygenated polymer side groups. In short, a type of Bolland[8] mechanism is operative.

The present work is concerned with the oxidative degradation of relatively thick (*ca.* 100 μ) polystyrene films in a temperature range from 249 to 300°. This range is beyond the softening point (*ca.* 230°) of this polymer, which is appreciably higher than that of the atactic polymer (*ca.* 83°).[9] Several of the parameters were measured as a function of time, such as oxygen uptake, increase in pressure, diffusion effects, peroxide formation, chain scission, and changes in ultraviolet spectra. Also chromatographic analyses of the products for the initial and final stages of the oxidation process were carried out. Because of the complexity of the processes involved and changes in diffusion rate, due to loss of weight and decrease in medium viscosity, only the very initial stages of the oxidation process can be evaluated quantitatively. The later stages can only be treated semiquantitatively. A diffusion-controlled mechanism, with respect to oxygen uptake by the film, is proposed in part II of this paper, which agrees satisfactorily with the experimental results for the initial stages of the oxidation process and with the trends of the later parts of the reaction.

Experimental Section

(a) Apparatus. Pressure measurements were carried out in quartz spoon-reaction vessels, which served at the same time as pressure gauges, actuating Statham transducers connected to Sanborn recorders. This arrangement was described previously.[10] Some of the reactions were performed in reaction vessels of similar shape and size as the spoon gauge; however, without spoon and pointer. The residual polymer was investigated spectrophotometrically at various times (Beckman spectrophotometer, Model DB-6). Dioxane was used as solvent and solutions were measured in 1-cm quartz cells. The spoon gauges and any other reaction vessels were submerged for the desired time intervals in metal baths,[10] which were constant within ±1°.

Oxygen was determined according to a method by Sweetser.[11] The relevant apparatus was slightly modified. The method is based on a color reaction using methylviologen.

Intrinsic viscosities were measured with a semimicro Cannon-Ubbelodhe viscometer (No. 50) at 30 ± 0.04°.

Chromatography of the liquid residue after prolonged oxidative degradation was carried out in an Aerograph, Autopret Model A-700. The column consisted of a 10% Carbowax, 20M on Haloport F (aluminum column 0.25 in. × 6 ft). The injection block had a temperature of 335° and the Detector a range of 330–350°. The carrier gas was helium (40 ml/mm), the attenuation by one or by one-eighth; the column temperature varied for different experiments from 100 to 238°.

(b) Materials. Isotactic polystyrene was obtained from the Dow Chemical Co. The sample (batch No. 759-32-10) contained 20% w/w of atactic polymer. Two samples were prepared. The first was purified without removal of the atactic component by repeated precipitation with methanol from benzene solution. The second sample was purified in the same way as the first and the atactic polymer was removed by methyl ethyl ketone. The first sample had an intrinsic viscosity of $[\eta] = 2.22$ dl/g in benzene solution and $[\eta] = 2.53$ dl/g in chloroform solution at 30°. The second sample had an $[\eta] = 3.32$ dl/g in chloroform as solvent, also at 30°. The latter, being a better solvent than benzene, was used in all experiments.

Ultrahigh pure oxygen was obtained from Matheson Co. All other chemicals were of the purest grades available.

(c) Procedures. Isotactic polystyrene (10 mg) was deposited by evaporation of chloroform solutions at the inside walls of the respective reaction vessels. The films were evacuated (10^{-5} mm) for at least 24 hr. After the desired time period of oxidation, the reaction vessels were dipped into cold 10% w/v HNO_3; this arrested the reaction and also removed any metal from the bath clinging to the outside wall of the reaction vessel. It has been pointed out above that oxygen was determined according to a method elaborated by Sweetser.[11] The apparatus is shown in Figure 1. A polymer film was deposited and the respective amount of oxygen was introduced. The vessel was then sealed at point a. The concentration of oxygen after the reaction was determined by measuring the absorbance at 580 mμ before and after breaking of vessel A. Calibration curves were obtained in the same apparatus. Peroxides were ascertained by a spectrophotometric method according to Eiss and Giesecke;[12] benzoylleucomethylene blue was the

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[8] J. L. Bolland, *Quart. Rev.* (London), 3, 1, (1949), see also J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236, 244 (1946); H. H. G. Jellinek, *Appl. Polym. Symp.*, No. 4, 41 (1967); G. S. Scott, "Atmospheric Oxidation and Antioxidants," Elsevier Publishing Co., New York, N. Y., 1965.

[9] A. Ledwith, *Ind. Chem.*, **37**, 71 (1961).

[10] H. H. G. Jellinek and J. E. Clark, *Can. J. Chem.*, **41**, 355 (1953).

[11] P. Sweetser, *Anal. Chem.*, **38**, 979 (1967).

[12] M. I. Eiss and P. Giesecke, *ibid.*, **31**, 1558 (1959).

reagent, which reacts with peroxide; the absorbance was measured at λ 662 mμ. The reagent was kindly supplied by National Cash Register, Inc.

The increase in pressure as a function of time was measured with the spoon gauge: $\Delta P_t = P_{\text{volatiles},t} \neq (P_{O_2,t} - P_{O_2,i})$; here ΔP_t is the pressure difference between the pressure at time t and the initial pressure, $P_{\text{volatiles},t}$ is the pressure due to volatile products and $P_{O_2,t}$ the oxygen pressure, both at time t; $P_{O_2,i}$ is the initial oxygen pressure, which was taken as zero (base) line.

Chain scission was followed by intrinsic viscosity measurements in chloroform solutions. The sample was assumed to have initially a random molecular size distribution. This was confirmed by the fact that samples, which suffered more than six breaks for each original polymer molecule, gave straight lines by plotting $1/\overline{DP}_{n,t}$ *vs.* time, which extrapolated back to the original molecular weight.

All determinations were carried out as a function of initial oxygen pressure, temperature (249–300°), and time. A number of experiments were also carried out with polymer films of different thickness, but having the same surface area as all other samples.

Number average molecular weights of the sample were calculated, assuming random distributions. The relation used is as follows: $[\eta] = (2.95 \times 10^{-4}\bar{M}_n) \times 0.734$ dl/g, where $\bar{M}_n$ is the number average molecular weight.

As already pointed out, uv absorption spectra were measured in dioxane solution in 1-cm cells. After oxidation, the residual sample was completely soluble.

Results

I. Initial Stages of Oxidative Degradation (100% Isotactic Polystyrene). First, it was ascertained that chain scission or volatile formation did not occur in absence of oxygen in the relevant temperature range (249–300°) for at least 10 min.

Figures 2–4 show typical curves for the initial stages of pressure increase (ΔP), oxygen consumption, and peroxide formation as a function of time, initial oxygen pressure (measured at 22°), and temperature, respectively. The relevant amounts are expressed in moles referred to 1 ml of polymer film. The oxygen pressure and the concentration of tertiary hydrogen atoms can be considered practically constant during these initial stages. All experiments were carried out in quartz spoon gauges or quartz vessels of similar shape and size. Polymer film (10 mg) was deposited by evaporation from chloroform solution for each experiment.

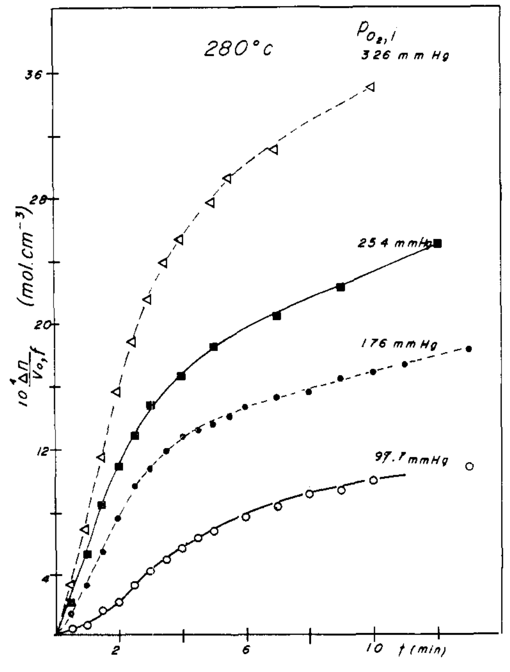

Figure 2. Initial stages of pressure increase as function of time for the thermooxidative degradation of isotactic polystyrene at 280°. Initial oxygen pressures (measured at 22°) are indicated.

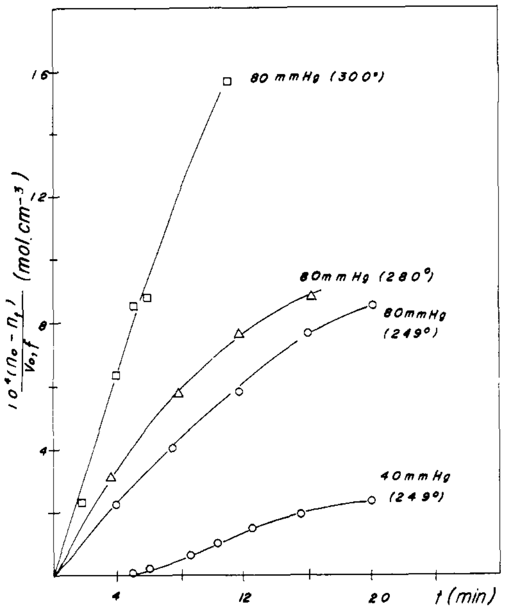

Figure 3. Oxygen consumption as function of initial oxygen pressure and temperature (number of moles of O_2 consumed for each volume unit (cm^3) of polymer film).

The slopes $K_{\Delta P}$ for all straight line parts derived from all experiments, except for peroxide formation, were measured. In the case of peroxide formation, the rate equation derived for the proposed mechanism (see part II) has been used for this purpose ($d[\text{ROOH}]_f/dt = K_{\text{ROOH}} - C[\text{ROOH}]_f$; rate plotted *vs.* $[\text{ROOH}]_f$).

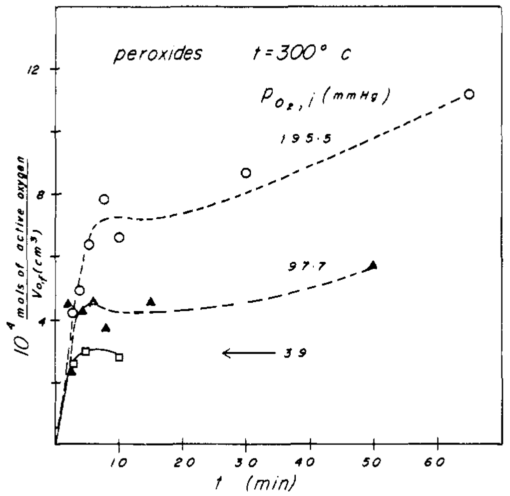

Figure 4. Peroxide concentration (moles of active oxygen/cm^3 of film) as a function of initial oxygen pressure at 300°. The appearance of linearity of the initial curves is due to the "contracted" time scale.

TABLE I

		249°	280°	300°
Pressure increase	$K_{\Delta P}'$ (mol min^{-1} cm^{-3} mm^{-1})	0.47×10^{-6}	2.1×10^{-6}	4.8×10^{-6}
Oxygen consumption	K_{r,O_2}' (mol min^{-1} cm^{-3} mm^{-1})	0.66×10^{-6}	1.05×10^{-6}	1.97×10^{-6}
Peroxides	K_{ROOH}' (mol min^{-1} cm^{-3} mm^{-1})			1.97×10^{-6}
	C' (min^{-1} mm^{-1})			$\sim 3.7 \times 10^{-3}$

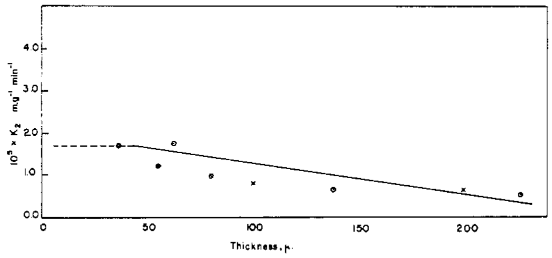

Figure 5. Slopes of second straight lines for different film thicknesses ($10^5 K_2$ moles g^{-1} min^{-1}; compare Figure 2, $P_{O_2,i}$ = 176 mm, 280°); ⊙ Ronel, × Lipovac.

The constants K_{ROOH} and C, respectively, were found to be linearly proportional to $P_{O_2,i}$. The film volumes were obtained by a short extrapolation of a density *vs.* temperature curve.[13]

The various K and C values plotted as a function of initial oxygen pressure give straight lines for each temperature. The straight lines for 300° are not as satisfactory as those for the lower temperatures. The slopes of these straight lines, which are the rates for unit initial oxygen pressure, are given in Table I.

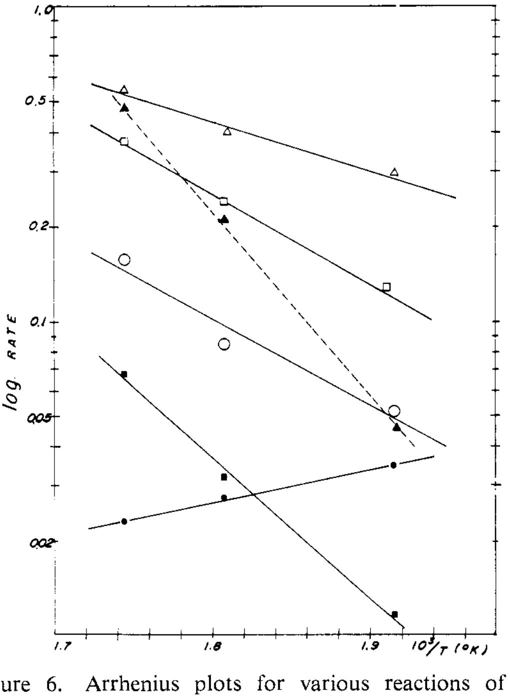

Figure 6. Arrhenius plots for various reactions of the thermooxidative degradation of isotactic polystyrene: —●—, chain scission log ($10^4 K_{CS}$) at 39 mm initial oxygen pressure; —■—, volatile formation log (10^4 K'_{vol}) at 1 mm; —○— O_2 consumption log (10^3 K_{r,O_2}) at 80 mm; —□—, peroxide formation log ($10^3 K_{ROOH}$) at 195.5 mm; —△—, peroxide decomposition log (C) at 195.5 mm; ---▲---, pressure increase log (10^{-5} $K'\Delta_P$) at 1 mm.

Experiments were carried out with films of different thickness but constant surface areas. The results for the slope of the second straight line parts (see Figure 2, 176 mm, 280°) are plotted *vs.* film thickness in Figure 5. The slopes decrease directly proportional with increase in film thickness, indicating diffusion control even below 100 μ film thickness.

Arrhenius equations were derived for the various rates and are shown in Figure 6. They are

pressure increase, initial rate

$$K_{\Delta P}' = 1.98 \times 10^5 e^{-27700/RT}$$

oxygen consumption

$$K_{r,O_2}' \; 9.2 \times 10^{-2} e^{-12300/RT}$$

peroxide formation (equation derived for $P_{O_2,i}$ = 195.5 mm)

$$K_{ROOH} = 35.2 e^{-13770/RT}$$

peroxide decomposition (equation derived for $P_{O_2,i}$ = 195.5 mm)

$$C = 2.2 \times 10^2 e^{-6900/RT} \text{ min}^{-1}$$

All rates are in mol min^{-1} cm^{-3} mm^{-1}, except for K_{ROOH} and C. Chromatographic analysis of volatiles produced during the initial stages showed that predominantly water is produced. The column used was ($^1/_8$ in. × 6 ft.) 5% tricresyl phosphate on 60/80 Chromoport (temperature of column 50°, detectors 180°, injector 105°, respectively).

II. Chain Scission. Chain scission for the initial stages obeys the empirical equation (see Figure 7)

$$\alpha = \frac{1}{\overline{DP}_{n,t}} - \frac{1}{\overline{DP}_{n,0}} = K_{\exp} t$$

Here α is the degree of degradation, $\overline{DP}_{n,t}$ and $\overline{DP}_{n,0}$ the number average chain lengths at t and t = 0, respectively. The number average molecular weights

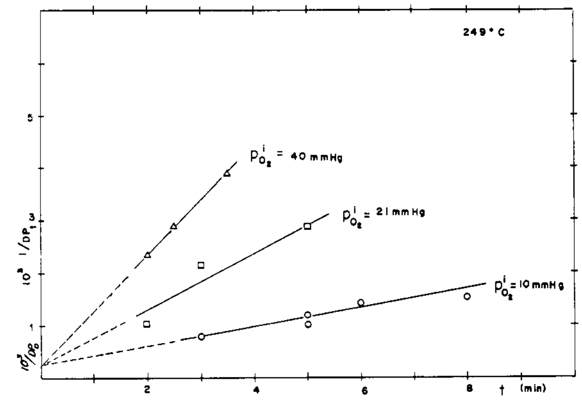

Figure 7. $1/DP_{n,t}$ as function of initial oxygen pressure and time at 249°.

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[13] G. Natta, F. Danusso, and G. Moraglio, *Makromol. Chem.*, **28**, 166 (1958).

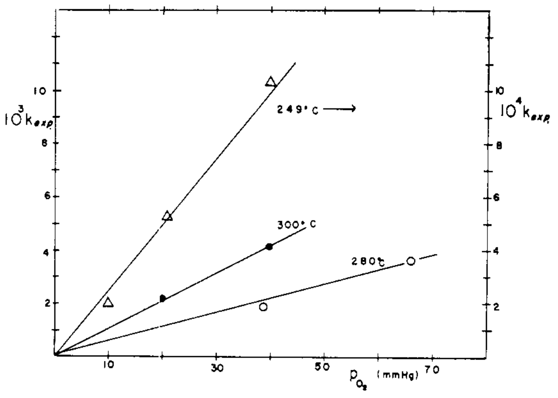

Figure 8. Experimental rate constants (min^{-1}) as function of initial oxygen pressure and temperature.

were obtained as follows. After more than six breaks in each original chain, the sample will have practically a random molecular size distribution. For such a distribution, the relationship that is obeyed[14] is $[\eta] = (2.59 \times 10^{-4}\,\bar{M}_n) \times 0.734$ dl/g. Here $\bar{M}_n$ is the number average molecular weight. As Figure 7 shows, the straight lines extrapolate back satisfactorily to initial chain lengths, calculated on the assumption that the initial molecular size distribution is also random. The rate constants increase linearly with the initial oxygen pressure (see part II of this paper) as shown in Figure 8, and the energy of activation for K_{exp} is 17.2 kcal/mol.

III. Uv Spectra. Uv spectra as a function of initial oxygen pressure and oxidation time are shown in Figure 9. Initially, an increase in absorbance as well as a change in characteristic shape take place.

The initial rates, K_{A} (min^{-1} mm^{-1}), obtained from the maximum absorbances $A_{1\mathrm{cm}}{}^{1\%}$at λ 245 mμ were 0.11, 0.35, and 0.78 at 249, 280, and 300°, respectively.

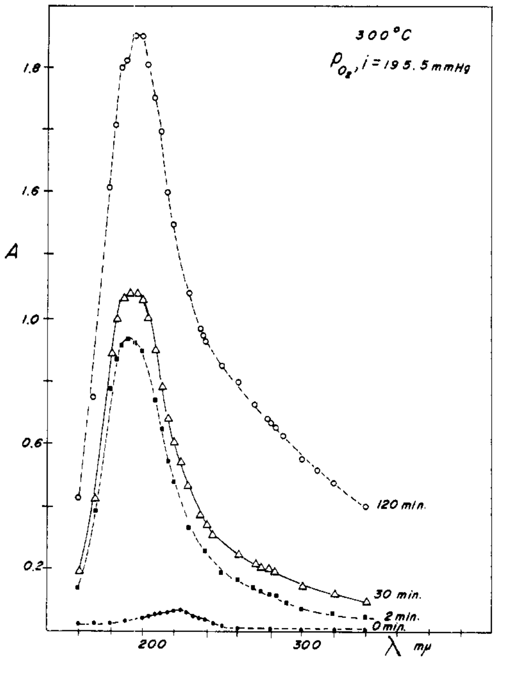

Figure 9. Uv spectra of isotactic polystyrene in dioxane solution before and after oxidative degradation as a function of time at an initial oxygen pressure of 195.5 mm and at 300°.

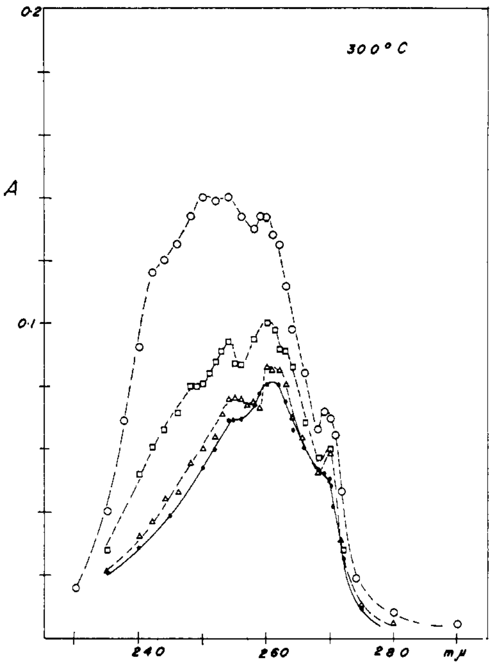

Figure 10. Uv spectra of isotactic polystyrene in dioxane solution after thermal degradation under vacuum at 300°: -△-△-△-, after 20 min; -□-□-□-, after 30 min, -○-○-○-, after 120 min (-●-●-, 0 min.).

The relevant Arrhenius equation is $K_{\mathrm{A}} = 5 \times 10^8 e^{-23100/RT}$ min^{-1} mm^{-1}. A slight increase in overall absorbance occurs after 20 min exposure in absence of oxygen at 300°. The K_{A} value for this thermal degradation is $K_{\mathrm{A}}' = 2 \times 10^{-4}$ min^{-1} mm^{-1}—much smaller than the corresponding values obtained in the presence of oxygen. Prolonged thermal degradation (absence of oxygen) under vacuum at 300° causes profound changes in the spectra. The characteristic polymer spectrum disappears (see Figure 10).

IV. Degradation of Isotactic Polystyrene Containing 20% of Atactic Isomer. Samples of isotactic polystyrene containing 20% w/w of atactic polymer were also degraded. The atactic component seems to degrade quite fast (see Figure 11). Chain scission

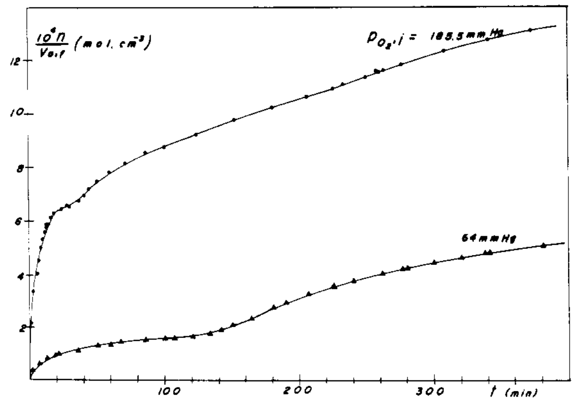

Figure 11. Pressure increase as a function of time and initial pressure at 250° for isotactic polystyrene containing 20% atactic isomer. Initial amount of polymer is 24 mg. 65 mm O_2—$10^4\Delta K\Delta_{\mathrm{P}}$ = 0.016 mol cm^{-3} min^{-1}; 185.5 mm O_2—$10^4\Delta K\Delta_{\mathrm{P}}$ = 0.78 mol cm^{-3} min^{-1}.

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(14) T. Ogihara, S. Tsuchiya, and K. Kuratani, *Bull. Chem. Soc. Jap.*, **38**, 978 (1965).

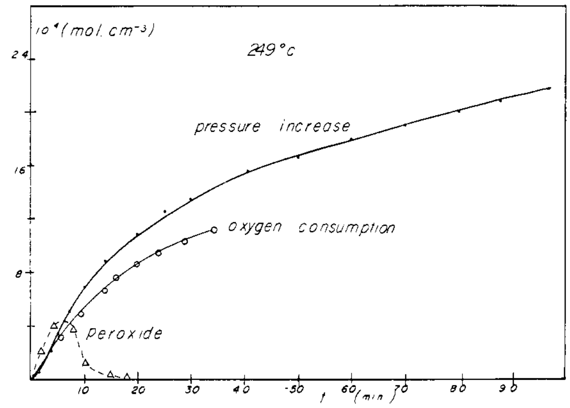

Figure 12. Typical curves for pressure increase ($P_{O_2,i}$ = 192 mm), oxygen consumption ($P_{O_2,i}$ = 80 mm), and peroxide concentration ($P_{O_2,i}$ = 195.5 mm) in the film for extended periods of time of thermooxidative degradation of isotactic polystyrene at 249°.

measurements of this sample ($[\eta]_0$ = 2.53 dl/g at 30° in $CHCl_3$) degraded at 250° and initial oxygen pressure of 39 mm show a straight line relationship of $1/DP_{n,t}$ *vs.* time up to 6 min; the initial slope is 1.0×10^{-4} min^{-1}.

V. Later Stages of the Oxidation Process. Figures 12 and 13 show some typical examples of the increase of pressure *vs.* prolonged periods of time. The pressure increases eventually pass over into straight lines. The Arrhenius equation for this part of the process is given by $K_{L,\Delta P}' = 4.98 \times 10^2 e^{-16200/RT}$ mol min^{-1} cm^{-3} mm^{-1}. Also oxygen consumption and peroxide concentration are shown in Figures 12 and 13. Chromatograms for the final stages of oxidation for either polymer are given in Figures 14a and b. These will be discussed in part II; appreciable amounts of water are being produced during the initial oxidation process.

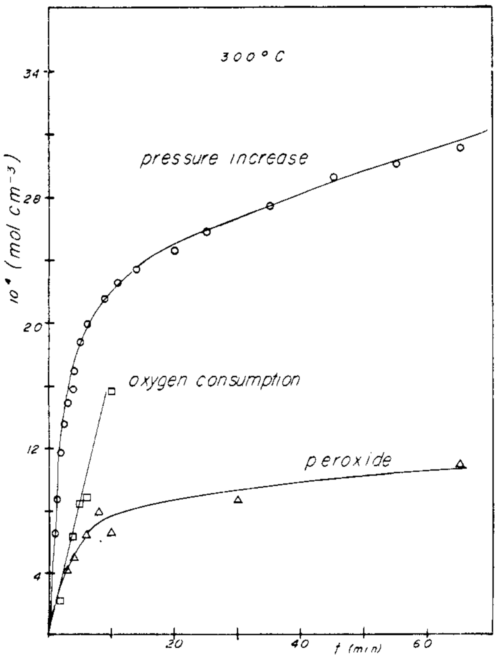

Figure 13. Pressure increase ($P_{O_2,i}$ = 195.5 mm); oxygen consumption ($P_{O_2,i}$ = 80 mm), and peroxide concentration ($P_{O_2,i}$ = 195.5 mm) for thermooxidative degradation at 300°.

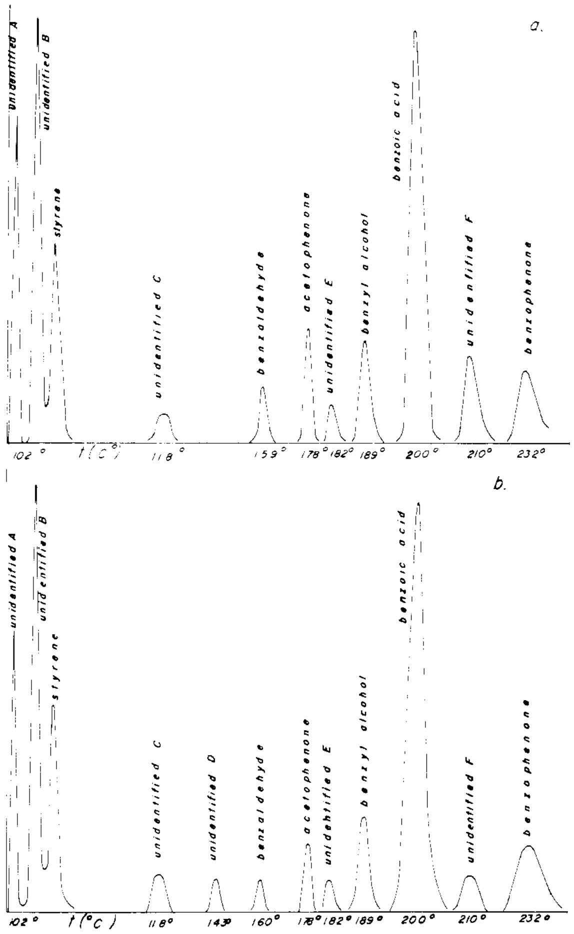

Figure 14. Chromatograms of (a) isotactic and (b) atactic polystyrene residue after prolonged thermooxidative degradation at 300°. Residues are of liquid-like consistency; injection volume 25 μl. Rate of temperature change 9.25° min^{-1} (linear programming).

Discussion

The relatively low energy of activation for oxygen consumption, 12.3 kcal/mol, and the results obtained for different film thickness (Figure 5), indicate that the oxidation process is controlled by the diffusion of oxygen into the polymer film. Such diffusion control was also found for the oxidation of polyethylene films above a certain film thickness;[15] the energy of activation in the latter case is about 12.5 kcal/mol.[2] Grieveson and coworkers[16] found an energy of activation of 15 kcal/mol for the oxidation of fine polyethylene powder at about 200°; this was assigned to diffusion as rate-determining step. Isotactic polystyrene was studied in the present work and it must be pointed out again that its softening point lies at about 230°, whereas the one for the atactic isomer is *ca.* 83°; isotactic polystyrene is, of course, much more crystalline than

(15) B. S. Biggs, National Bureau of Standards Circular 525, U. S. Government Printing Office, Washington, D. C., 1953, p 137.

(16) B. M. Grieveson, R. N. Haward, and B. Wright in Thermal Degradation of Polymers, S. C. I. Monograph No. 13, 1961, p 413.

the atactic isomer. Both these factors decrease the film thickness at which oxidation becomes diffusion controlled.

As diffusion of oxygen into the film is the rate-controlling step and if it is assumed that a type of Bolland mechanism[8] is operative, then the initial stages of the oxidation process can be accounted for quantitatively. This will be demonstrated in part II of this paper. The amount of tertiary hydrogen atoms in the film and the initial oxygen pressure can be considered approximately constant for the initial stage of the oxidation reaction. The later stages of this process, however, become too complicated to be explained quantitatively; at best a semiquantitative account can be given and trends can be indicated. Volatiles produced by chain scission alone will consist only of quite small amounts during the initial stages. The volatiles formed during this initial stage must be almost exclusively due to decomposition of hydroperoxide groups, which does not lead to chain scission. Actually, the main volatile product during the initial stage appears to be water.

As the oxidation proceeds beyond its initial stage, the oxygen pressure in the gas phase, the film thickness, and the medium viscosity decrease continuously; the latter decrease is due to chain scission. It may even be the case that eventually the chemical reaction will become rate determining.

Acknowledgment. The authors with to thank the U. S. Army Office of Research, Durham, N. C., for a Grant No. DA-ARO-D-31-124-G984, which made this work possible. Thanks are also due to Dr. S. H. Ronel for carrying out experiments with polymer films of different thickness (see Figure 5).

Diffusion-Controlled Oxidative Degradation of Isotactic Polystyrene at Elevated Temperatures.
II. Kinetics and Mechanism

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Received May 1, 1969

ABSTRACT: The initial stage of the oxidation process can be accounted for by diffusion control of the oxidation rate of polymer to hydroperoxide. The kinetics of the initial oxidation reaction follows quantitatively a type of Bolland mechanism. Chain scission consists of a random process due to hydroperoxide decomposition. Energies of activation have been determined for all the reactions involved in the oxidative process. The kinetics and diffusion equations for the initial stage of the oxidation are well obeyed by the experimental results. Later stages of the reaction can only be described in a qualitative or at best semiquantitative way.

Experimental results of the oxidative degradation of isotactic polystyrene were presented in part I of this paper.[1] It was pointed out there that the reaction is diffusion controlled and follows some type of Bolland mechanism. The complexity of the process becomes very large after the very initial stages, as oxygen pressure, film thickness and medium viscosity (chain scission) decrease continuously. Thus, it is only feasible to treat the very initial stages of the oxidation process quantitatively, whereas trends can only be pointed out for later stages.

The present part of the paper deals with a quantitative evaluation of the experimental results obtained during the initial stages of the thermooxidative degradation process. It has already been pointed out that the reaction is diffusion controlled. The relevant diffusion equations are given here. Not as much use could be made of these equations as desired, since nothing is known about gas concentration gradients in the polymer at the temperatures employed here; but they give general guidelines about the reactions involved and are generally applicable under experimental conditions as encountered here.

Later parts of the oxidation process are discussed only briefly due to their complexity.

A. Initial Stages of Oxidation. Only initial stages of the oxidation process will be considered here, where the oxygen pressure and the amount of tertiary hydrogen atoms can be considered practically constant. This is a good approximation for the experiments carried out at 249 and 280°, respectively; however, it is still quite satisfactory at 300°, as only the first 6–8 min are involved. The decrease in oxygen pressure is 7% at 249°, 10% at 280°, and 25% at 300° at the end of the initial stages considered here.

A mechanism can be formulated, which accounts satisfactorily and in a quantitative way for the initial stages of the oxidation process. Here $O_{2,g}$ denotes

$$\text{slow} \qquad O_{2,g} \xrightarrow[\text{into film}]{\overset{D_{O_2}}{\text{diffusion}}} O_{2,f}$$

oxygen in the gas phase and $O_{2,f}$ oxygen in the film, respectively; D_{O_2} is the diffusion coefficient for O_2

$$\text{fast} \quad \left\{ \begin{array}{l} RH + O_{2,f} \xrightarrow{k_1} R\cdot + HO\cdot_2 \\ R\cdot + O_{2,f} \xrightarrow{k_2} RO\cdot_2 \\ RO\cdot_2 + RH \xrightarrow{k_3} ROOH + R\cdot \end{array} \right.$$

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(1) Part I: H. H. G. Jellinek and S. N. Lipovac, *Macromolecules*, 3, 231 (1970).