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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Iring, M. , Földes, E. , Szesztay, M. and Tüdös, F.(1990) 'Thermal Oxidation of Partially Hydrogenated Poly-2,3 Diphenylbutadienes and Polystyrenes', *Journal of Macromolecular Science, Part A*, 27: 13, 1657 – 1671

To link to this Article: DOI: 10.1080/00222339009351508

URL: <http://dx.doi.org/10.1080/00222339009351508>

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THERMAL OXIDATION OF PARTIALLY HYDROGENATED POLY-2,3-DIPHENYLBUTADIENES AND POLYSTYRENES†

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INTRODUCTION

Oxidative degradation of industrial polystyrene with a head-tail structure (H-T PS) initiated with different energy sources is a well-studied subject [1]. It should be remarked, however, that the results are often controversial. This can perhaps be explained by the different experimental conditions—quality of polymer samples, technical details, physico-chemical variables, etc.—applied intentionally or circumstantially. On the other hand, the oxidative stability of head-head PS (H-H PS) has scarcely been investigated.

†This paper is based on cooperative work with Professor Otto Vogl on the comparative autoxidation of head-to-head and head-to-tail polyolefins and poly(vinyl halides).

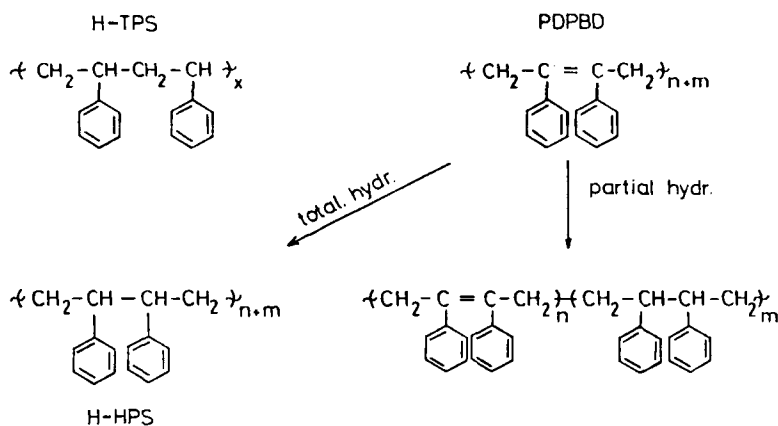


FIG. 1. Polymers investigated.

Recently we started a study on the oxidative properties of poly-2,3-diphenylbutadiene (PDPBD), the predecessor of H-H PS, partially hydrogenated PDPBD, hydrogenated PDPBD, e.g., H-H PS, and a commercial PS type.

Our aim is to contribute to the results available in the literature and to get new information on the kinetics and mechanism of oxidation of styrene polymers of different structures, and then use them for elucidation of the effect of H-H structure as well as of double bond concentration on the oxidation process.

Some of our initial results are presented in this paper.

EXPERIMENTAL

Polymers

The structures of the polymers investigated are shown in Fig. 1.

Commercial polystyrene with the trade name Krasten 144 was used as H-T PS and was purified as follows: 100 mL benzene was added to 4 g polystyrene and the mixture was heated under a reflux condenser on a water bath for 10 min. The polymer was precipitated into 1000 mL methanol, then filtered, dried in vacuum, and sieved. The procedure was repeated two times. The samples other than H-T PS were synthesized by E. Földes based on the method described in Refs. 2 and 3 and used

Table 1. Characteristics of the Samples^a

No.	Sample	n		m		Polydispersity $M_n \times 10^{-5}$	T_s , °C
		$n + m$	$n + m$	$n + m$	$n + m$		
1.	PDPBD	1.00	0.00	4.19	1.45	233.5	
2.	PDPBD/73	0.27	0.73	4.92	1.40	270.5	
3.	PDPBD/94	0.06	0.94	3.58	1.49	286.5	
4.	H-H PS	0.01	0.99	3.86	0.93	287.5	
5.	H-T PS			2.54	0.94	288.0	

^a T_s = starting temperature of the weight loss in the TG curve.

without further purification. 55 μm thick hot-pressed polymer films were prepared in order to investigate their oxidation.

Some characteristics of the samples are presented in Table 1.

Oxidation Technique and Conditions

Thermal oxidation was carried out in equipment [4] suitable to follow the kinetics of oxygen absorption. Conditions of oxidation: temperature, 140–190°C; oxygen pressure, 100 kPa; film thickness, 55 \pm 10 μm .

Methods

Methods presently applied for the characterization of untreated and oxidized samples are summarized in Table 2.

Mass change was measured in a thermobalance of the Mettler TA 3000 system. Molecular mass distribution (MMD) was determined on a Waters ALC-GPC-201 equipped with two detectors: RI 400 and UV-440 with a filter for 254 nm [6].

Table 2. Methods of Investigation

Property	Method/Reference
Kinetics of oxygen uptake	Gas volumetric [4]
Concentration of functional groups	IR analysis [5]
Mass change	Thermal analysis
Molecular mass change	GPC [6]

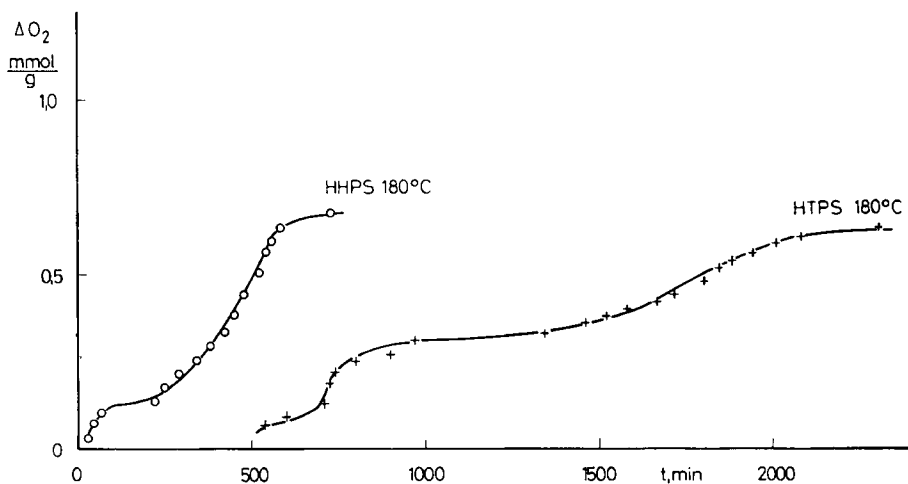


FIG. 2. Kinetics of oxygen uptake of head-head and head-tail polystyrenes.

RESULTS

Oxygen Uptake

Characteristic kinetic curves of oxygen uptake of H-H PS and H-T PS samples are shown in Fig. 2. The curves are more complex than those of a common autocatalytic oxidation. The kinetics of oxygen uptake generally shows 4 stages in most cases: an induction period of a certain length, then a fast uptake of a small amount of oxygen, followed by an accelerating oxygen uptake, and at the end the process slows down remarkably.

The kinetics of oxygen uptake of PDPBD and the partially and totally (e.g., H-H PS) hydrogenated PDPBD samples can be seen in Fig. 3. In contrast to the saturated polymers investigated, PDPBD shows a decelerating kinetic curve, e.g., the maximal rate of oxygen uptake is at $t = 0$. The partially hydrogenated samples show transitional behavior between the saturated and unsaturated polymers.

IR Spectra

The IR spectra qualitatively reflect the change in the chemical structure of oxygenated polymers. Oxygen-containing functional groups with

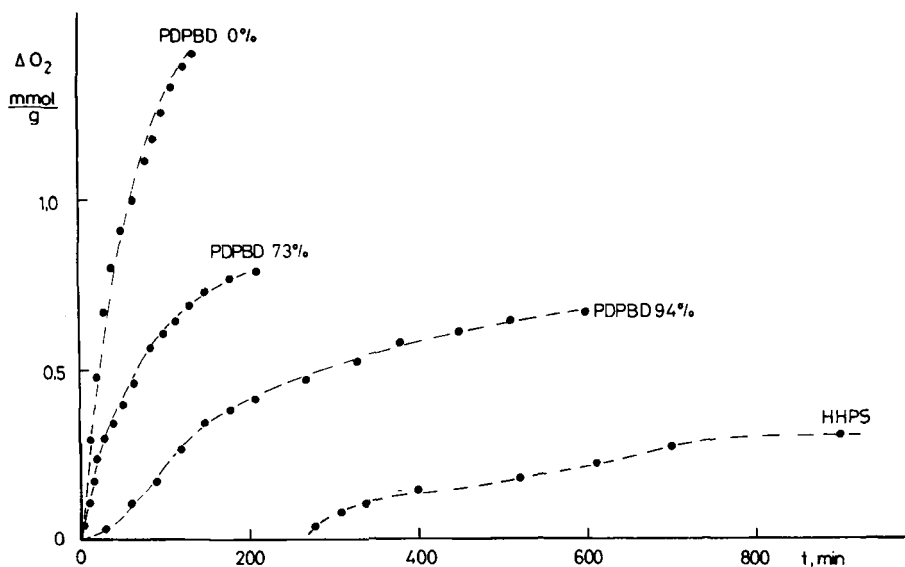


FIG. 3. Kinetics of oxygen uptake of poly-2,3-diphenylbutadienes hydrogenated to different extents.

both different and similar structures have been detected in the polymers investigated, as is shown by the characteristic IR spectral regions in Fig. 4. A rather sharp absorption with a peak maximum at 1684 cm^{-1} appears in the spectra of every polymer, and this can be attributed to acetophenone-like structures according to the literature. A more complex absorption peak can be seen in the wavelength range $1780\text{--}1700\text{ cm}^{-1}$, indicating the formation of carbonyl groups other than acetophenone. The shape of the peak and its relative intensity compared to that at 1684 cm^{-1} change with the structures of the polymers.

The differently bonded —OH groups of the saturated polystyrenes give IR absorption in the $3600\text{--}3500\text{ cm}^{-1}$ region, while those of the unsaturated polymer give a broad band at $3600\text{--}3300\text{ cm}^{-1}$.

The partly hydrogenated samples are transitions between the saturated and unsaturated structures.

Absorptivities characteristic for acetophenone structures (A_{AP}) were studied as a function of oxygen uptake (ΔO_2).

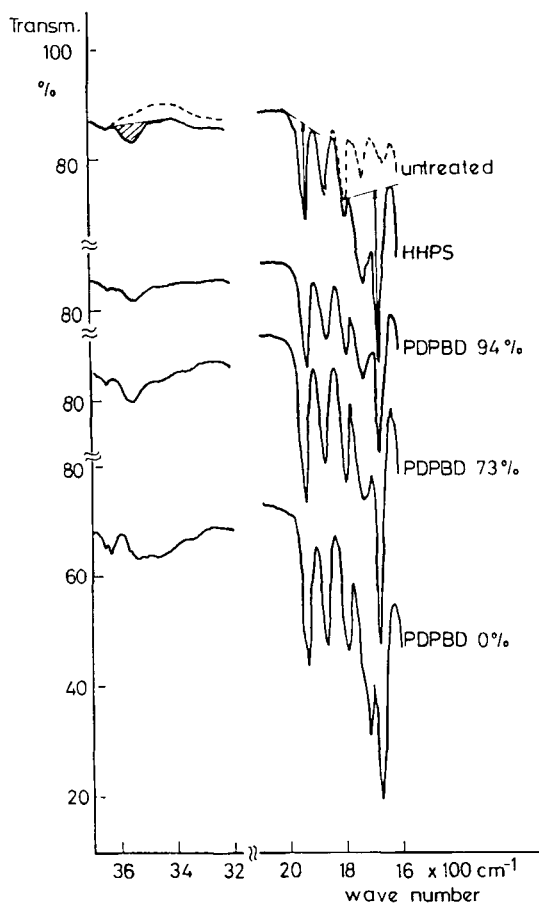


FIG. 4. Characteristic IR spectra regions of the polymers investigated.

$$A_{AP} = \lg \left[\frac{I_0}{I} \right]_{1684 \text{ cm}^{-1}}$$

The A_{AP} values were related to A_{Pol} , the characterizing polymer concentration, where

$$A_{Pol} = \lg \left[\frac{I_0}{I} \right]_{1944 \text{ m}^{-1}}$$

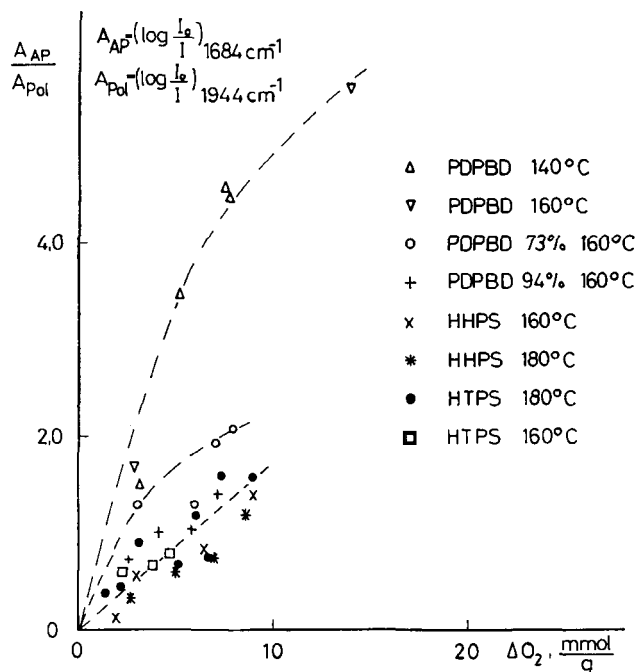


FIG. 5. Absorbance characterizing the amount of acetophenone structures formed in the oxidation of polymers as a function of overall oxygen uptake.

The A_{AP}/A_{Pol} vs ΔO_2 correlations are shown on Fig. 5 for every polymer.

Molecular Mass Distribution

The MMD curves of the untreated and oxidized polymers were taken in a GPC instrument equipped with both RI and UV detectors. The average number of scissions was evaluated from the \bar{M}_n values derived from the MMD curves. The s values obtained with the two detectors are shown as a function of ΔO_2 in Fig. 6.

DISCUSSION

Thermal oxidation of the investigated polymers is a complex process

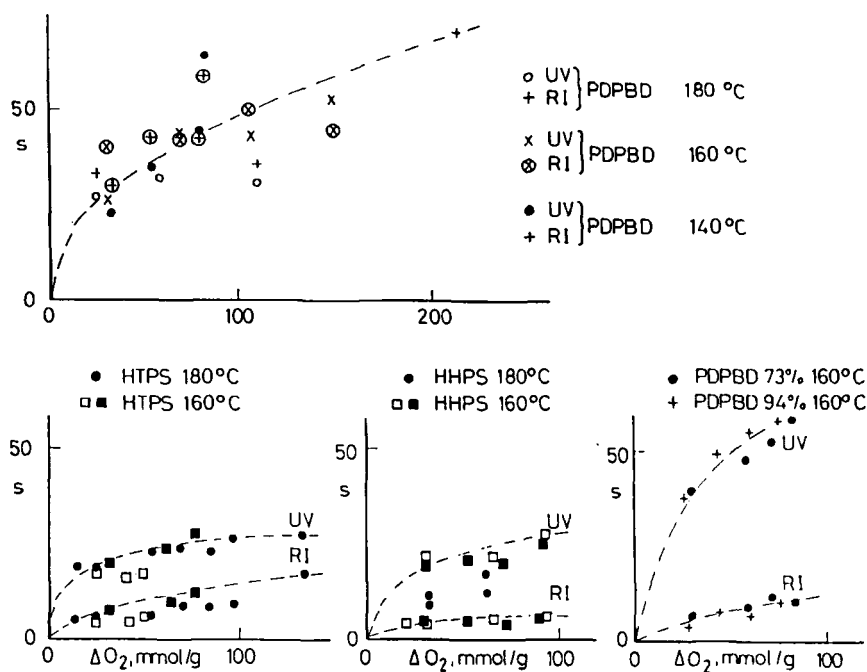


FIG. 6. Average number of scissions (s) detected by UV and the RI method as a function of overall oxygen uptake.

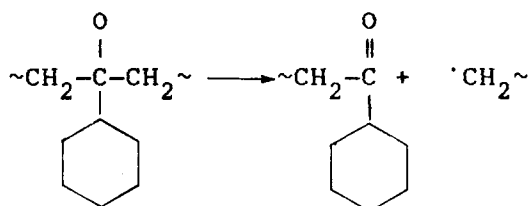
including many elementary reaction steps and it is therefore not easy to follow technically.

Nevertheless, it is highly probable that the initial step stage, which often appears on the kinetic curves of oxygen uptake, results in rather fast oxidation of the weak links in the polymer chain. A similar phenomenon was observed and interpreted by Grassie and coworkers who studied the thermal degradation of PS [7-9]. As mentioned above, the oxidation kinetics and mechanism of PDPBD, the predecessor of H-H PS, differ from those of the saturated polymer. The rate of oxidation of PDPBD is several times higher than that of H-H PS, and the slackening of the process is probably due to the decrease of double bond concentration rather than to autoinhibition as found in the case of PS (see Fig. 3).

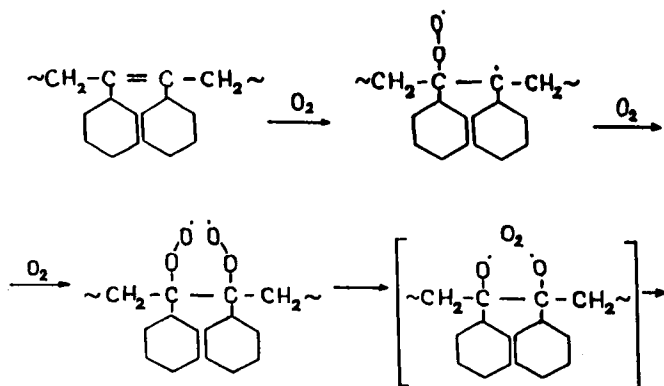
A correlation was found between the initial rate of oxidation and the degree of unsaturation. This means that the vinylic-type weak links of the PS chain can cause an increase in the initial rate of oxidation compared to the saturated structure.

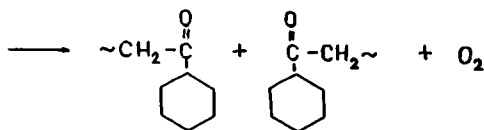
The A_{AP}/A_{Pol} vs ΔO_2 correlations in Fig. 5 show that the amount of acetophenone structures formed from identical amounts of oxygen is approximately the same in the cases of H-H PS, H-T PS, and PDPBD/94, while it is much higher in PDPBD. The PDPBD/73 sample, i.e., PDPBD hydrogenated to the extent of 73%, represents a transition between unsaturated and nearly or totally saturated polymers.

It is assumed that hydroperoxide groups are formed along the chain (PSHP) in the thermal oxidation of PS, although opinions in the literature concerning the possibility of detecting those groups are controversial. In any case, the decomposition of $-OOH$ groups of PSHP leads to the formation of the alkoxy radical which can transform, resulting in breaking of the polymer chain and formation of acetophenone structures:



In the case of PDPBD, 2 mole equivalents of acetophenones can be formed per 1 mole oxygen consumed:





This or a similar mechanism is most probably responsible for the much higher $A_{\text{AP}}/A_{\text{Pol}} \cdot \Delta\text{O}_2$ values in the case of PDPBD.

Authors who have studied the thermal oxidation of PS are in agreement concerning the existence of PSHP as one of the active intermediates of the process. This point was even proved by Dulog and coworkers in an indirect way [10].

There is a divergence of opinion concerning the detectability of PSHP. Beachell and Smiley [11] stated the PSHP is undetectable; Gol'dberg and coworkers detected it and studied its concentration in thermal oxidation [12]. As shown in Fig. 4, various $-\text{OH}$ structures are formed in the oxidation of polymers with different structures. The IR absorption observed in the $3600\text{--}3500\text{ cm}^{-1}$ range in the cases of H-T PS and H-H PS might be caused by $-\text{OOH}$ groups, so we tried to decompose these supposed $-\text{OOH}$ groups by heating the oxidized samples for 2 h at 170°C in vacuum. The spectra of H-T PS before and after heating are shown in Fig. 7. The spectrum of oxidized H-T PS did not change with heating. Neither a decrease in absorption in the $-\text{OH}$ range nor an increase in absorption in the $=\text{CO}$ range ($=\text{CO}$ is the probable product of decomposition of $-\text{OOH}$) could be observed. We also tried to detect $-\text{OOH}$ groups in H-T PS by the chemical methods described in Ref. 5, but without success. It was therefore concluded that the energy absorption of PS at $3600\text{--}3500\text{ cm}^{-1}$ is caused by $-\text{OH}$ -containing structures other than $-\text{OOH}$. The identification of those structures and the extension of the investigation to other polymers and conditions are in progress.

Both coupling and scission of macroradicals occur in thermal oxidation. As a result, the formation of an insoluble gel and smaller molecules of different lengths can be observed. We studied the MMD of the soluble part of the polymer samples. The average number of scissions (s) detected by both UV and RI detectors as a function of ΔO_2 are shown in Fig. 6. It was observed that the ratio between the s values obtained by the two different methods, $s(\text{UV})/s(\text{RI})$, is approximately unity in the case of PDPBD while it is much higher in the case of other polymers.

As a technical consequence, it should be pointed out that the s value

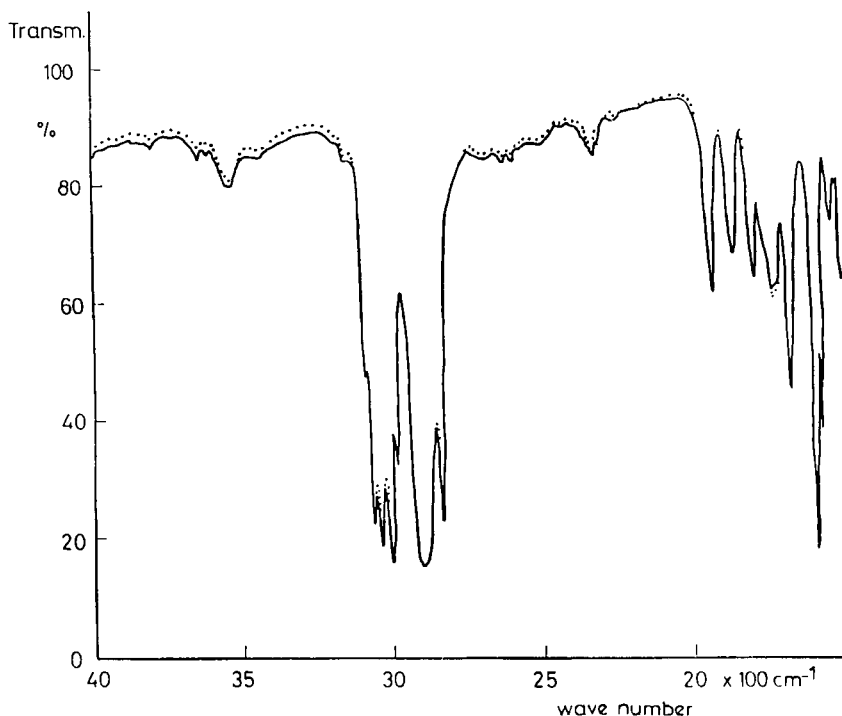


FIG. 7. IR spectra of oxidized H-T PS: before heating (—) and heated for 2 h at 170°C in vacuum(· · ·) ($\Delta O_2 = 0.92$ mmol/g polymer).

derived from the results obtained with the UV detector cannot be considered as a true measure of the degree of scission process.

On the other hand, these results give valuable information about the mechanism of oxidation.

The distribution of UV activity along the chain and the UV activity of the fragments must be even and proportional to the mass in the case of PDPBD. At the beginning, the mass proportional UV activity is related to the double bonds built in regularly into the chain. Some of the double bonds disappear in the course of oxidation. At the same time, however, UV active, oxygen-containing functional groups are formed. It seems that the resulting UV activity remains proportional to mass in

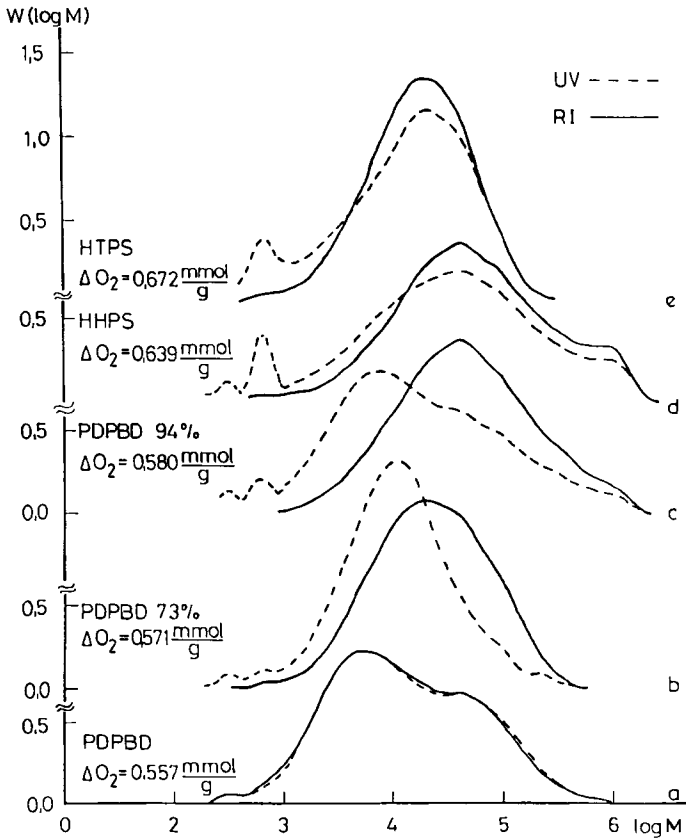


FIG. 8. MMD curves of oxidized polymers taken by RI and UV detectors.

the process, as proven by the MMD curves of oxidized PDPBD shown in Fig. 8(a).

The UV activities of the untreated polymers decrease strongly with a decrease of the double bonds, so the saturated polymers show a very small UV absorption (see Fig. 9).

In the course of oxidation, the formation of carbonyl groups and/or conjugated double bonds and other UV-active functional end-groups takes place. In this case the UV activity can show a reverse proportionality with the chain length if the same average number of UV-active groups is built into every chain. This means that the calculated MMD curves

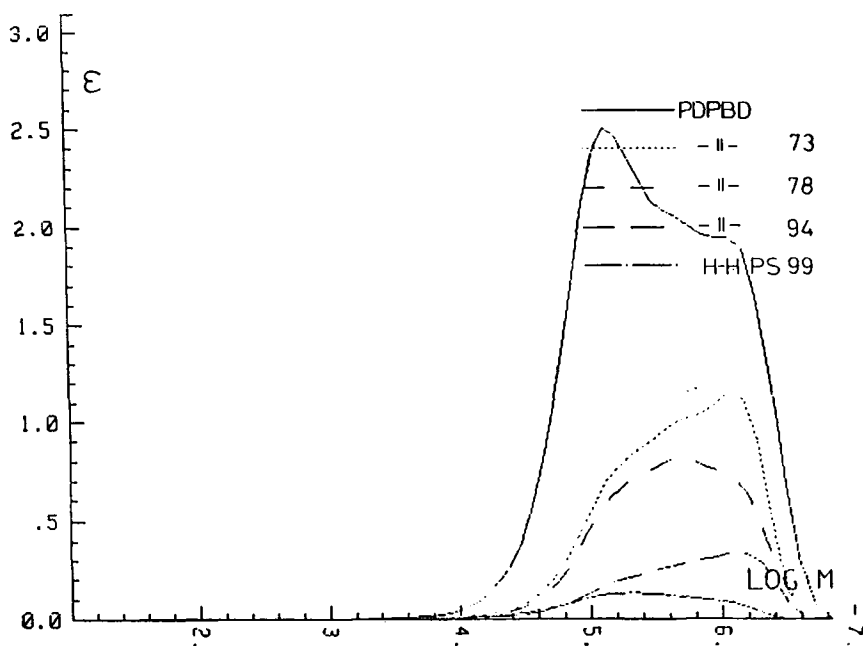


FIG. 9. UV absorption of the untreated polymers investigated at 254 nm as a function of $\lg M$.

will show a shift toward the smaller molecules, resulting in virtual \bar{M}_n and s data, the former smaller and the latter higher than that of the actual values. This phenomenon is well reflected in the MMD curves of the polymers as detected by both the UV and RI methods and shown in Fig. 8(b-e). The MMD curves of the saturated polymers (Fig. 8d, e) show definitely separated peaks with maxima of $\bar{M}_n \sim 630$ and in H-H PS of ~ 320 , even at a relatively small conversion. This means that these highly UV-active small molecules are formed in the initial stage of thermal oxidation.

Values of $s(\text{RI})$ and $s(\text{UV})$ are plotted against $A_{\text{AP}}/A_{\text{Pol}}$ in Fig. 10, resulting in curves similar to that of $s(\text{RI})$ and $s(\text{UV})$ vs ΔO_2 (see Fig. 6). The $s(\text{RI})$ vs $A_{\text{AP}}/A_{\text{Pol}}$ correlation can be represented to a reasonable approximation by a straight line going through the origin. The slow rate phase of the $s(\text{UV})$ vs $A_{\text{AP}}/A_{\text{Pol}}$ correlation can also be described by a straight line with a positive y -axis section.

It seems that most of the UV-active small molecules are formed in the

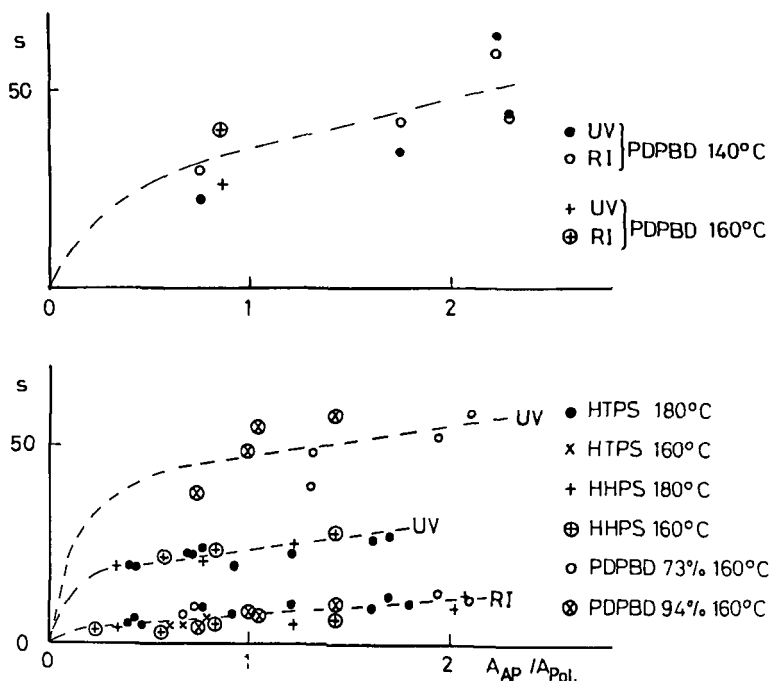


FIG. 10. $s(RI)$ and $s(UV)$ values of the different polymers as a function of A_{AP}/A_{Pol} .

initial stage of oxidation and are perhaps related to the reaction represented by the short, steep part observed in the kinetics of oxygen uptake, while in the following stages of the process the change in both UV activity and molecular length take place simultaneously.

SUMMARY

The thermal oxidation of poly-2,3-diphenylbutadiene (PDPBD), partially and totally hydrogenated PDPBD (the latter is head-head polystyrene, H-H PS) and a commercial head-tail polystyrene (H-T PS) has been investigated.

PDPBD shows a continuous decelerating kinetics of oxygen uptake, while H-H PS and H-T PS oxidize by complex accelerating-decelerating

kinetics. The partially hydrogenated samples show a transitional behavior between the saturated and unsaturated samples.

Acetophenone-like end groups, among others, are formed in the course of oxidation. The amount of those formed from an identical amount of oxygen is much higher in PDPBD than in saturated polymers. A mechanism has been suggested to interpret the results.

—OH groups of different structures are formed in the oxidation, which we found were not —OOH in the cases of H-T PS and H-H PS.

MMD curves of the soluble parts of oxidized polymers were taken with the aid of a GPC instrument equipped with both UV and RI detectors, and the average numbers of scissions [$s(\text{UV})$ and $s(\text{RI})$] were derived. $s(\text{UV})/s(\text{RI}) \approx 1$ was found for PDPBD, while a much higher ratio was obtained for the other polymers. As a consequence, the $s(\text{UV})$ values cannot be considered as true measures of the degree of scission process.

On the other hand, these results give valuable information about the mechanism of thermal oxidation.

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