

Photochemical Oxidation & Stabilization of Butyl Rubber in Solid State

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Thin films of butyl rubber in the temperature range of 265 to 293 K irradiated at 366 nm undergo random chain scission in air. Monochromatic quantum yields of photolysis for butyl rubber with and without incorporation of diphenylmercury have been compared. The rate of polymer bond rupture has been measured by change in weight average molecular weight. A method is described for the estimation of aldehyde groups in irradiated butyl rubber. The incorporation of 0.5% diphenylmercury in the matrix of the rubber film exercises a protective influence on the photolytic degradation of the rubber.

THE photochemical oxidation in solid state has been studied^{1,2} quantitatively for only a few copolymers at temperatures where thermal degradation is not significant. Studies on oxidation and stabilization in the presence of air have received even less attention³. Considerable insight into the nature of the photolytic processes can be obtained from the knowledge of quantum yield alone. The determination of this variable depends on the ability to measure the rate of polymer bond rupture and the rate of absorption of the energy which initiates bond rupture.

In the present investigation, the film of butyl rubber has been photodegraded and stabilized in the temperature range of 265 to 293 K in air by the light of wave-length 366 nm and the quantum yield for random chain scission determined. A chemical method is also described for the estimation of aldehyde groups in irradiated butyl rubber. This study on the photolysis also allows some speculation with regard to the mechanism of photodegradation and stabilization of butyl rubber containing different concentrations of diphenylmercury as a stabilizer.

Materials and Methods

Butyl rubber (BR), a copolymer of isobutylene and isoprene (M/s. Swastic Rubber Co., Poona) was purified by acetone and methanol extractions and kept in contact with petroleum ether (40-60°). The rubber was precipitated from 1% solution in petroleum ether with acetone. The incorporation of the diphenylmercury (DPM) was effected by dissolving the BR (5%) in cyclohexane containing 0.1, 0.5, 1.0 and 2.0% (wt/wt) of DPM. The BR films of uniform thickness were prepared by casting solutions (10 ml each) in cyclohexane containing BR with and without DPM on quartz plates which were sealed with pyrex glass plates having a 5 cm diameter bore. The films were dried *in vacuo* for 24 to 30 hr to a constant weight.

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Photo-irradiation—The photochemical oxidation was carried out in air with a 125 watt (230 V) mercury vapour lamp whose glass casing was removed. The dried BR films with and without DPM were irradiated with a monochromatic light of wavelength 366 nm for different intervals of time in the temperature range of 265-293 K. The temperature of the system was controlled within $\pm 0.5^\circ\text{C}$.

The intensity of radiation and quantum yields for polymer chain scissions were quantitatively determined by potassium ferri-oxalate actinometry⁴.

Molecular weight determination—The stock solutions of BR were prepared by dissolving the films in a known volume of distilled cyclohexane. In order to remove the suspended impurities from solution, it was centrifuged (15,000 rpm) for 1 hr. The supernatant solution from the tubes was withdrawn by means of a pipette and transferred into a filtering G5 sintered glass funnel directly. Solutions of different concentrations were obtained by adding a known volume of the stock solution to a known volume of the solvent in the light scattering cell. The Zimm plots have been employed to estimate the values of the weight average molecular weights as a function of time. The dissymmetry ratios have been utilized to calculate the particle scattering factors for correction of the light scattering data.

Refractive index increment (dn/dc)—The refractive index increment (dn/dc) with concentration of BR and the optical constant (H) for the solution in cyclohexane were determined using a Brice-Phoenix differential refractometer (Phoenix Precision Instrument Co., Philadelphia, USA) and the values at 298 K are: $dn/dc=0.13$; and $H=1.96 \times 10^{-6}$.

Estimation of aldehyde groups in irradiated BR—To irradiated BR film (0.2 g) dissolved in toluene (5 ml), was added 2,4-dinitrophenylhydrazine (DNP, 0.05 g) dissolved in THF (4 ml). After 24 hr, a drop of conc. hydrochloric acid was added and the solution flushed with nitrogen. The sealed tube was placed in a water-bath at 20°C and after 3 hr the rubber was precipitated by adding the solution drop by drop into ethanol (100 ml). The rubber

was pressed dry between filter papers, cut into small pieces, then redissolved in toluene (10 ml) and reprecipitated by adding into ethanol (150 ml). This procedure was repeated till unreacted DNP was removed. The rubber was finally dried *in vacuo*. A 0.4% to 0.6% solution of the DNP treated rubber was made in THF and the optical density measured in a 1 cm cell at 360 nm using a Beckman DU spectrophotometer. The blank was a solution of the original rubber treated similarly but without the DNP.

The calibration graph was obtained by adding known quantities of the 2, 4-dinitrophenylhydrazone derivative of acetaldehyde to 0.6% rubber solutions and measuring the optical density. The calibration curve was linear for —CHO concentrations up to 8×10^{-8} mol ml⁻¹. If the concentration of the DNP derivative of rubber = A (kg ml⁻¹), and the concentrations of —CHO groups corresponding to the optical density of the solution at 360 nm (from the graph) $10^{-8} B$ (mol ml⁻¹), concentration of —CHO group in rubber = (B/A) mol kg⁻¹.

Theoretical —UV irradiation of thin films of BR results in a rapid decrease in the molecular weight of the polymer. This behaviour is characteristic of a polymer undergoing random scission without extensive depolymerization. Under such conditions it can be assumed that the number of scissions occurring in a polymer chain is proportional to the number of quanta absorbed by that chain, the proportionality constant is the quantum yield for chain scission.

For a linear polymer having a number average molecular weight $M_{n(o)}$ initially and $M_{n(p)}$ after a random cleavage process, the average number of scissions (s) taking place in a polymer chain is given by Eq. (1).

$$[M_{n(o)}/M_{n(p)}] - 1 = [u_{1(o)}/u_{1(p)}] - 1 \quad \dots (1)$$

The degree of degradation is given by Eq. (2)

$$p = \frac{s}{u_{1(o)}} = \frac{1}{u_{1(p)}} - \frac{1}{u_{1(o)}} \quad \dots (2)$$

In Eqs (1) and (2) $u_{1(o)}$ is the initial number average degree of polymerization and $u_{1(p)}$ after degradation. The relationship between the number of chain bonds originally present n_o and $u_{1(o)}$ is given by Eq. (3) :

$$n_o = \frac{wN}{m} \frac{u_{1(o)} - 1}{u_{1(o)}} \quad \dots (3)$$

where w is weight of irradiated polymer, m is the molecular weight of the monomer and N is the Avogadro number. A similar equation can be written for the number of chain bonds, $n_{(p)}$ at (p) and $u_{1(p)}$:

$$n_{(p)} = \frac{wN}{m} \frac{u_{1(p)} - 1}{u_{1(p)}} \quad \dots (4)$$

When all the bonds in the polymer chains are broken by random degradation and each bond has equal strength and accessibility, the following relationship⁵ for the zero order reaction can be written :

$$-\frac{dn_{(p)}}{dt} = \Phi I_a \quad \dots (5)$$

where I_a is the light intensity absorbed in the polymer sample and Φ is the quantum yield. After integrating (5) we obtain :

$$n_{(p)} = n_{(o)} - \Phi I_a t \quad \dots (6)$$

A combination of Eqs (3), (4) and (6) gives :

$$\frac{1}{u_{1(p)}} = \frac{1}{u_{1(o)}} + \frac{m}{wN} \Phi I_a t \quad \dots (7)$$

The quantum yield Φ can be determined from Eq. (7) by plotting $1/u_{1(p)}$ vs irradiation time t . The ratio $u_{1(p)}/u_{1(o)}$ can be replaced by the ratio of weight average degree of polymerization $u_{2(p)}/u_{2(o)}$, without committing an appreciable error. These ratios can be conveniently determined by light scattering measurements.

Results and Discussion

Table 1 gives the values of time of irradiation, corresponding values of the weight average molecular weights $M_{w(p)}$, the ratios of $u_{2(p)}/u_{2(o)}$, the average number of chain scissions (s) and the degrees of degradation (p) for BR irradiated with and without DPM as a photostabilizer in air in the temperature range of 265 to 293 K with a light intensity 1.68×10^{-8} Einstein sec⁻¹ cm⁻² for different intervals of time. An inspection of the data in Table 1 reveals that at each temperature the values of p of the irradiated samples are greater in the absence of DPM than those in the presence of DPM. This indicates that DPM retards the oxidative degradation of BR.

Larger quantum yields are displayed by blank BR at all temperatures (Table 2). The smaller quantum yields are typical of BR in which the initial UV absorption occurs at phenyl radicals furnished by DPM to the molecules of BR. The quantum yields have values less than unity. This is evidently due to other processes which diminish the number of molecules formed by photo-dissociation. A possible explanation is that in a large molecule the energy is absorbed at one site but then the electronic excitation is partitioned over many bonds so that the probability of a single bond breaking is small, or the absorbed energy is dissipated by quenching reactions.

It has been observed that the quantum yields per chain scissions per absorbed photon decrease with increasing percentage of DPM incorporated in the matrix of BR films at 283 K. A saturation limit in photostabilization of BR by DPM is achieved beyond 0.5% by weight of DPM. The quantum yields for the chain scission of BR samples differing in weight average molecular weight indicate that there is a slight dependence on molecular weight and that random scission processes. The low values of quantum yields indicate that a polymer with DPM exhibits high photochemical stability and beyond a concentration of 0.5% DPM incorporated in the matrix of BR film affords complete protection from actinic deterioration. The experimental values of quantum yield are in good agreement with the values reported⁶ for polyisoprene, the part of the repeating unit of BR.

The results on the effect of irradiation time on the formation of degradation products are given in

TABLE 1 — PHOTOLYSIS OF BUTYL RUBBER IN THE ABSENCE AND PRESENCE OF VARIOUS CONCENTRATIONS OF DPM IN AIR AT DIFFERENT TEMPERATURES

[Light intensity flux at 366 nm = 1.68×10^{-8} Einstein $\text{sec}^{-1} \text{cm}^{-2}$]

Time of irradiation (sec $\times 10^{-3}$)	$M_w(p) \times 10^{-6}$	$u_2(p)/u_2(o)$	s	$p \times 10^5$	Time of irradiation (sec $\times 10^{-3}$)	$M_w(p) \times 10^{-6}$	$u_2(p)/u_2(o)$	s	$p \times 10^{-5}$
BUTYL RUBBER SYSTEM : TEMP. 293 K					BUTYL RUBBER + 2.0% DPM SYSTEM : TEMP. 283 K				
0.0	1.36	1.00	—	—	0.0	1.36	1.00	—	—
1.8	0.89	0.66	1.43	5.92	14.4	1.36	1.00	0.00	0.00
3.6	0.76	0.56	2.07	8.58	50.4	1.36	1.00	0.00	0.00
5.4	0.70	0.52	2.40	9.49	57.6	1.36	1.00	0.00	0.00
7.2	0.69	0.51	2.47	10.24	64.8	1.36	1.00	0.00	0.00
10.8	0.64	0.47	2.81	11.75					
14.4	0.64	0.47	2.81	11.75					
18.0	0.64	0.47	2.81	11.75					
21.6	0.62	0.47	2.96	12.25					
BUTYL RUBBER + 0.1% DPM SYSTEM : TEMP. 293 K					BUTYL RUBBER SYSTEM : TEMP. 273 K				
0.0	1.36	1.00	—	—	0.0	1.36	1.00	—	—
7.2	1.25	0.93	0.24	1.31	7.2	0.94	0.66	1.39	5.76
10.8	1.20	0.89	0.38	1.56	14.4	0.84	0.61	1.71	7.09
14.4	1.18	0.81	0.44	1.81	21.6	0.80	0.59	1.85	7.65
21.6	1.05	0.80	0.64	2.09	28.8	0.79	0.58	1.91	7.93
43.2	0.96	0.81	0.44	1.89	36.0	0.78	0.57	1.95	8.08
					43.2	0.77	0.56	1.98	8.22
					50.4	0.77	0.56	1.99	8.25
					57.6	0.76	0.55	2.02	8.37
BUTYL RUBBER SYSTEM : TEMP. 283 K					BUTYL RUBBER + 0.1% DPM SYSTEM : TEMP. 273 K				
0.0	1.36	1.00	—	—	0.0	1.36	1.00	—	—
7.2	0.77	0.52	2.36	8.22	21.6	1.16	0.95	0.13	0.52
14.4	0.70	0.51	2.41	9.97	36.0	1.09	0.81	0.67	2.76
21.6	0.65	0.48	2.78	11.54	50.4	1.09	0.81	0.67	2.76
36.0	0.63	0.47	2.87	11.58					
39.6	0.62	0.46	2.96	12.27					
BUTYL RUBBER + 0.1% DPM SYSTEM : TEMP. 283 K					BUTYL RUBBER SYSTEM : TEMP. 265 K				
0.0	1.36	1.00	—	—	0.0	1.36	1.00	—	—
7.2	1.30	0.96	0.13	0.52	14.4	1.04	0.77	0.86	3.56
21.6	1.20	0.89	0.38	1.56	21.6	0.99	0.73	1.05	4.34
32.4	1.18	0.81	0.44	1.81	43.2	0.89	0.66	1.43	5.92
36.0	1.18	0.81	0.44	1.81	50.4	0.88	0.65	1.47	6.08
BUTYL RUBBER + 0.5% DPM SYSTEM : TEMP. 283 K					BUTYL RUBBER + 0.1% DPM SYSTEM : TEMP. 265 K				
0.0	1.36	1.00	—	—	0.0	1.36	1.00	—	—
14.4	1.34	0.99	0.01	4.15	14.4	1.31	0.96	0.12	0.50
36.0	1.36	1.00	0.00	0.00	25.2	1.25	0.93	0.24	0.99
57.6	1.36	1.00	0.00	0.00	28.8	1.25	0.89	0.38	1.56
64.8	1.36	1.00	0.00	0.00	50.4	1.25	0.93	0.24	0.99
BUTYL RUBBER + 1.0% DPM SYSTEM : TEMP. 283 K					57.6	1.30	0.95	0.13	0.52
0.0	1.36	1.00	—	—	64.8	1.31	0.96	0.12	0.50
14.4	1.35	0.99	0.01	4.15					
43.2	1.36	1.00	0.00	0.00					
57.6	1.36	1.00	0.00	0.00					
64.8	1.36	1.00	0.00	0.00					

TABLE 2 — VALUES OF QUANTUM YIELDS FOR PHOTO-OXIDATIVE DEGRADATION AND STABILIZATION OF BUTYL RUBBER IN THE ABSENCE AND PRESENCE OF DPM IN AIR AT DIFFERENT TEMPERATURES

Temp. K	$\Phi \times 10^4$ (Chain scissions per absorbed photon)	
	BR	BR + 0.1% DPM
293	4.77	0.87
283	2.31	0.58
273	1.37	0.30
265	0.46	0.06

Table 3. Though the estimated aldehyde content is slightly higher for BR in the absence of DPM, there is considerable degradation of rubber. These results do not show whether the reaction is complete, that is, whether DNP reacts with all the aldehyde groups in rubber. It is not unreasonable to assume that almost complete reaction would occur since a great excess of DNP is used. The estimation of the aldehyde content with DNP in a sample of rubber by Percy *et al.*⁷ gave a value close to that found by this method.

Table 4 gives the results of carefully repeating the measurements six times on the same sample of rubber. The reproducibility is not particularly good, and

TABLE 3 — VARIATION OF ALDEHYDE CONTENT OF IRRADIATED BUTYL RUBBER (BR) WITH OR WITHOUT DPM

Time of irradiation hr	Aldehyde content ($\times 10^3$ mol kg ⁻¹ rubber)	
	BR	BR + 1% DPM
1	5.04	4.59
2	4.67	4.40
3	4.84	4.67
4	4.90	4.79

TABLE 4 — REPRODUCIBILITY OF THE METHOD : VALUES OF SIX REPLICATE MEASUREMENTS

Estimation No.	Aldehyde content ($\times 10^3$ mol kg ⁻¹ rubber)	Estimation No.	Aldehyde content ($\times 10^3$ mol kg ⁻¹ rubber)
1	4.11	4	3.75
2	3.90	5	3.82
3	4.19	6	3.98

Mean = 3.96×10^{-3}
 S.D. = 0.156
 Coefficient of variation = 3.94%

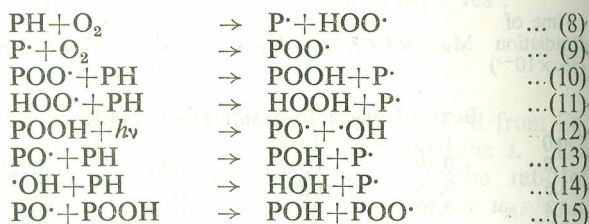
the results can differ by as much as 10% between measurements. This is not completely unexpected considering the low concentration of aldehyde groups. The error probably arises mainly from the loss of a small and variable amount of low molecular weight rubber during the purification procedure.

Mechanism of photo-degradation and stabilization of BR — It is now more or less established^{8,9} that the oxidative degradation of polymers proceeds through the formation of hydroperoxides. The hydroperoxides are formed as the primary products of oxidation which undergo a variety of reactions depending upon its structure and the reaction conditions. Hydroperoxidation takes place at a site requiring the least energy for the rupture of a C—H bond. The oxygen molecule acts like a diradical and is incorporated as such without the rupture of the $\ddot{O}-\ddot{O}$ bond. The σ bonded skeleton of the hydrocarbon does not undergo any change upto this stage. Chain-scission may take place subsequently depending upon the rupture of the hydroperoxide bond.

BR contains a small percentage of isoprene units which are distributed at random along with polymer chain and provide active sites for degradation. The methylenic hydrogen in the α -position to the double bond is a potential site for hydroperoxidation. The hydroperoxide formed may lead to chain-scission. This is further supported by the fact that the rate of chain-scission increases with the increase in unsaturation in the main chain of polymer. Thus the rate-controlling step in all these photo-oxidative processes may be the unimolecular decomposition of the hydroperoxide.

The decomposition of hydroperoxides into free radicals make an important contribution to the oxidation rate, and hence, any reaction which would in-

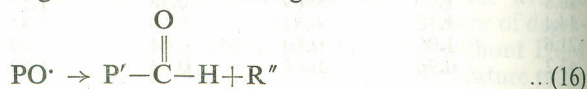
duce decomposition of these intermediates into non-radical products would contribute to stabilization. As shown in Scheme 1 for BR (PH) oxidation, radicals formed by hydroperoxide homolysis initiate new oxidative chains.



(induced decomposition)

Scheme 1

Reaction (12) may lead to chain scission through the process of H-transfer reaction and even a comparatively small extent of chain scission leads to a large change in molecular weight.

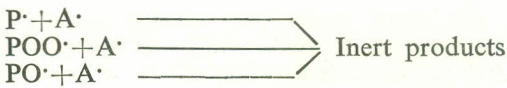


It is evident that stabilization of BR with DPM can be effected at several stages in this mechanism : Chain terminators function in the propagation stage (reactions 9-11) by competing with substrate molecules for the propagating radicals. However, the most effective chain terminators interrupt oxidation only after several propagation steps have occurred so that hydroperoxides still form in the inhibited reaction, although at a reduced rate. The chain termination of BR by DPM may also be involved in reactions which generate free radicals and compete therefore with reaction (16). DPM is also effective at the chain-branching stage by inducing decomposition of the hydroperoxides into inert products incapable of initiating new oxidative chain.

It can be seen¹⁰ that the energy required for bond scission (Hg-C) in DPM is much less than the energy carried by a photon of wavelength 366 nm (equivalent to 78.33 kcal mol⁻¹). The net result of incorporation of DPM is the production of phenyl radicals in the matrix of the polymer film on irradiation.

From the absorption spectra of irradiated DPM, one can see that with increasing period of irradiation, the concentration of phenyl radicals increase in cyclohexane solution. The increase in absorbance is linear with the dose indicating the absence of reverse reactions. These experiments indicate that irradiated DPM yields a strongly absorbing radical which acts as an inner filter for UV light. The absorbed light energy must be disposed by internal degradation processes to vibrational energy.

The hot phenyl radicals would tend to react with radicals formed by the chain scission due to the decomposition of P-O-O-H. All kinds of possibilities exist. Let A \cdot be any of the free radicals formed by the photolysis of DPM, then the formation of inert products can be visualized as shown in Scheme 2.



Scheme 2

The phenyl (A[·]) radical stabilized by resonance should not react further to initiate new oxidative chains. In solid state the excited species P[·] and A[·] would be energetic and long-lived, particularly where bimolecular collisions are required. Thus, in the present case where the reactions have been carried out in solid state, radicals may be unable to escape through the closely packed molecules that surround them. Most of them may recombine, dissipating the energy of recombination as heat and producing no overall chemical change.

Therefore, it appears that DPM acts via the mechanism of production of free radicals which terminate the chain reaction through radical-radical reaction, and by absorbing harmful UV radiation and dissipate the energy as harmless IR radiation or heat.

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