

Quantum Yield of Photolytic Degradation of Poly(1-Butene)

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ABSTRACT

Thin films of isotactic poly(1-butene) irradiated with a monochromatic light of 253.7 nm undergo random chain-scission in air in the temperature range of 267.0-313.0 °K. Quantum yields in the absence and presence of different stabilizers have been determined using a potassium ferrioxalate actinometer from 0.0188 to 0.00027 scissions per absorbed photon. Quantum yields for scission were independent of intensity. Light scattering technique was used to determine the rate of links breaking for polymeric systems. A saturation limit in photostabilization of isotactic poly(1-butene) by the stabilizers was achieved beyond 0.8, 0.7, 0.6 and 0.5 wt.% of copper(II) bis(1,3-diphenyltriazine-N-oxide) [CPTO], 1,3-diphenyltriazine-N-oxide [HPTO], o-phenanthroline bis(1,3-diphenyltriazine-N-oxide)cobalt(II) [CPTCO] and 2,4-diphenyl-6-(2'-hydroxyphenyl)-s-triazine [PHPT], respectively in the matrix of polymer film.

INTRODUCTION

The photolytic degradation of polyolefins in the solid state has been studied quantitatively for only a few materials at temperatures where thermal degradation is not a significant process. Degradation and stabilization process in the presence of atmospheric oxygen have received less attention. The quantum yield measurements can be used to determine the rate of polymer bond rupture and the absorption rate of the initiation energy. Quantum yields for chain scission have been reported for poly(α -methylstyrene) by STOKES et al. (1962), poly(methyl isopropylketone) by WISSBRUN (1959) and for butyl rubber by BHATNAGAR et al. (1977) and CHANDRA et al. (1979) but little attention has been paid to isotactic poly(1-butene).

In the present paper, we have reported the quantitative estimation of the quantum yields for the chain scission using a potassium ferri-oxalate actinometer. PARKER (1953) used this actinometer over the commonly used uranyl oxalate actinometer on the grounds that it is more sensitive and convenient at the longer wavelengths.

CHANDRA et al. (1980a and 1980b) and SINGH et al. (1981) have shown that incorporation of 2,4-diphenyl-6-(2'-hydroxyphenyl)-s-triazine 1,3-diphenyltriazine-N-oxide, copper(II) bis(1,3-diphenyltriazine-N-oxide) and o-phenanthroline bis(1,3-diphenyltriazine-N-oxide)cobalt(II) in the matrix of polymer film retard photooxidative degradation of isotactic poly(1-butene) by ultraviolet radiation. We have also determined the optimum concentration of different stabilizers which would achieve a saturation limit in photo-stabilization of poly(1-butene) against exposure to 253.7 nm ultra-violet radiation. Beyond a definite concentration of the different stabilizers incorporated in the poly(1-butene) film matrix offered complete protection from the photo-degradation.

EXPERIMENTAL

Materials: Isotactic poly(1-butene) [IPB] was supplied by Mobil Chemical Co., Metuchem, New Jersey, U.S.A. Traces of atactic part were removed from the sample according to the procedure of NATTA et al. (1956). The polymer sample was washed with ether and dried in vacuo. All the four used stabilizers were synthesized according to the following literature procedures:- 1,3-Diphenyltriazine-N-oxide [HPTO] according to SOGANI et al. (1956), copper(II)-bis(1,3-diphenyltriazine-N-oxide) [CPTO] according to SYAMAL et al. (in press), o-phenanthroline bis(1,3-diphenyltriazine-N-oxide)cobalt(II) [CPPTO] according to DUTTA et al. (1975) and 2,4-diphenyl-6-(2'-hydroxyphenyl)-s-triazine [PHPT] according to TITHERLEY et al. (1911). These stabilizers were characterized in our laboratories.

Procedures:- A 125 W (230 V) mercury vapour lamp was used as the source of light whose glass case was removed. SINGH et al. (1981) have described the method of IPB film preparation, the incorporation of the stabilizers in film matrix and its dissolution in cyclohexane. The dried IPB films were irradiated with a monochromatic light of 253.7 nm wavelength for different interval of times in the temperature range of 267-313 °K. The temperature of the system was controlled within $\pm 1^\circ\text{C}$. CHANDRA et al. (1976) have determined the weight average molecular weight ratio at any irradiation time to the initial molecular weight by light scattering technique.

Actinometry:- Potassium ferri-oxalate actinometer discovered by CALVERT et al. (1966), is very sensitive within the range of wavelengths from 253.7 nm to 578 nm, can measure smaller changes and is easy to use. For actinometric measurement 0.006M ferri-oxalate solution was used. Total filtered output of the mercury vapour lamp from 253.7 nm monochromatic filter and polymer film, was

measured by potassium ferri-oxalate solution in the quartz cell of known volume. The Fe^{3+} ions are reduced to Fe^{2+} by the irradiation of light. The product $\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$ does not absorb incident light and the Fe^{2+} ions can be determined colorimetrically as a complex with 1,10-phenanthroline.

RESULTS AND DISCUSSION

Ultra-violet irradiation of IPB films result in a rapid decrease in weight average molecular weight of the polymer with time. This type of behaviour is characteristic of a polymer undergoing random scission without extensive de-polymerisation. It can be assumed here that in a polymer the number of chain scission is proportional to the number of quanta absorbed by the chain, the proportionality constant being the quantum yield for chain scission.

If the polymer has a number average molecular weight, $M_{n,o}$ initially and $M_{n,t}$ after a random degradation process then the average number of scission(s) is:

$$(M_{n,o}/M_{n,t})^{-1} = (p_{n,o}/p_{n,t})^{-1} \quad (\text{i})$$

then the degree of degradation (\mathcal{L}) is

$$\mathcal{L} = \frac{s}{p_{n,o}} = \frac{1}{p_{n,t}} - \frac{1}{p_{n,o}} \quad (\text{ii})$$

where $p_{n,o}$ is the initial number average degree of polymerization and $p_{n,t}$ after degradation. The relation between the number of chain bonds originally present n_o and the number average degree of polymerization, $p_{n,o}$ is given by:

$$n_o = \frac{wN}{m} \frac{p_{n,o}^{-1}}{p_{n,o}} \quad (\text{iii})$$

where w is the weight of irradiated polymer, m is the molecular weight of the monomeric unit, N is the Avogadro number. We can write a similar equation for the number of chain bonds, $n(\mathcal{L})$ at \mathcal{L} and $p_{n,t}$:

$$n(\mathcal{L}) = \frac{wN}{m} \frac{p_{n,t}^{-1}}{p_{n,t}} \quad (\text{iv})$$

if all the bonds are broken by random degradation in the chains of polymer and each bond has equal strength and accessibility then JORTNER (1959) postulated the following relationship for the zero order reaction:

$$-\frac{dn(a)}{dt} = \phi I_a \quad (v)$$

where I_a is the light intensity absorbed in the polymer film and ϕ is the quantum yield.

$$I_a = I_o - I_t \quad (vi)$$

I_o is the intensity of incident light at the film and I_t is the intensity of transmitted light from the film. The intensity of the light beam I_o is evaluated by the equation:

$$I_o = \frac{n_{Fe^{2+}}}{\phi_{Fe^{2+}} t (1-10^{-\epsilon_{Fe^{3+}}} C_{Fe^{3+}})} \text{ quanta/sec.} \quad .. (vii)$$

where $n_{Fe^{2+}}$ is the number of the ions of Fe^{2+} formed after irradiation, t is the time of irradiation in seconds, and $\phi_{Fe^{2+}}$ is the quantum yield of Fe^{2+} at 2537 Å and $(1-10^{-\epsilon_{Fe^{3+}}} C_{Fe^{3+}})$ is the fraction of incident light absorbed by the Fe^{3+} compound and ≈ 1 .

$n_{Fe^{2+}}$ is determined colorimetrically by the equation:

$$n_{Fe^{2+}} = \frac{6.023 \times 10^{20} V_1 V_3 \log_{10} (I_o/I)}{V_2 l \epsilon} \quad (viii)$$

where V_1 is the volume of actual irradiated solution of potassium ferri-oxalate, V_2 is the volume of aliquot taken for analysis, V_3 is the final volume of aliquot to which V_2 is diluted, $\log_{10} I_o/I$ is the measured optical density of the solution at 5100 Å, l is the path-length of colorimeter tube and ϵ is the experimental value of the molar extinction co-efficient of the Fe^{2+} complex as determined from the slope of the calibration graph. On

integration eq. (v) gives:

$$n(\mathcal{L}) = n_0 - \phi I_a t \quad (\text{ix})$$

A combination of equations (iii), (iv) and (ix) gives:

$$\frac{1}{p_{n,t}} = \frac{1}{p_{n,o}} + \frac{m}{wN} \phi I_a t \quad (\text{x})$$

The quantum yield ϕ , can be determined from equation (x) by plotting $1/p_{n,t}$ versus irradiation time. The $p_{n,t}/p_{n,o}$ ratio can be replaced by the ratio of weight average degree of polymerisation $p_{w,t}/p_{w,o}$, without an appreciable error. These ratio can be conveniently determined by light scattering measurements.

Figure 1 shows that the plots are linear for small degree of degradation and then tends to increase. This figure gives the values of M_w versus irradiation time for IPB with and without the stabilizers at 283.0°K. It is clear from the plots that in the early stages of photo-degradation, random chain scission process takes place but for longer periods of irradiation crosslinking takes place. Thus chain scission and crosslinking are taken place simultaneously.

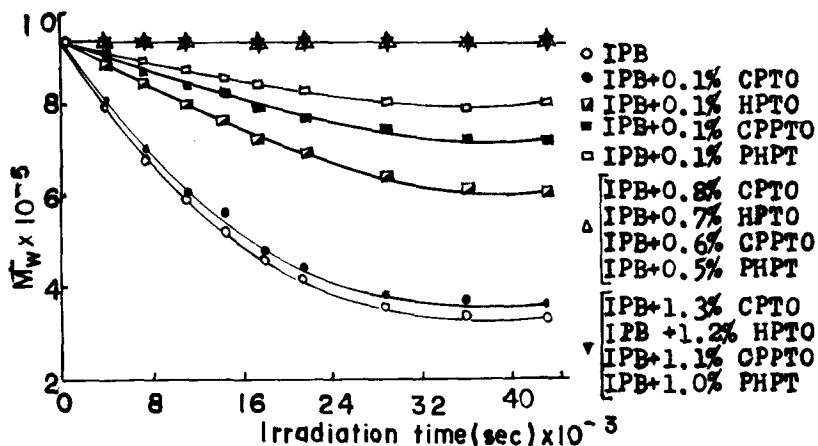


Fig. 1. Variation of \bar{M}_w of IPB vs time in absence and presence of various cons. of the stabilizers at 283°K.

The quantum yield variation per absorbed quantum in the absence and presence of different concentrations (by wt.) of CPTO, HPTO, CPPTO and PHPT as a function of temperature is given in Table 1. It can be seen from Figure 2 and Table 1 that the quantum yields per chain scissions per absorbed photon decrease with increasing percentage of the stabilizers incorporated in the IPB film matrix. A saturation limit in photostabilization of IPB by the stabilizers is achieved beyond 0.8, 0.7, 0.6 and 0.5 percent by weight of CPTO, HPTO, CPPTO and PHPT respectively.

The observed quantum yields have less values than unity. This means that the number of moles of degradation products are less than the number of photon absorbed by the polymer. This is because of that the absorption of energy occurs at one site in a macromolecule which is then partitioned over many bonds so that the single bond breaking possibility is small, or the dissipation of absorbed energy occurs by quenching reactions.

It is also observed that larger quantum yields are displayed by IPB without the stabilizers which is internally photo-sensitized, on the other hand, the smaller quantum yields are typical of IPB in which the initial ultra-violet absorption occurs at the stabilizers present in the matrix or IPB films. These low values of quantum yields indicate that a polymer with the stabilizers would exhibit photo-chemical stability and beyond the above stated optimum concentrations of the stabilizers incorporated in the IPB films afforded almost complete protection from actinic deterioration in the order CPTO < HPTO < CPPTO < PHPT.

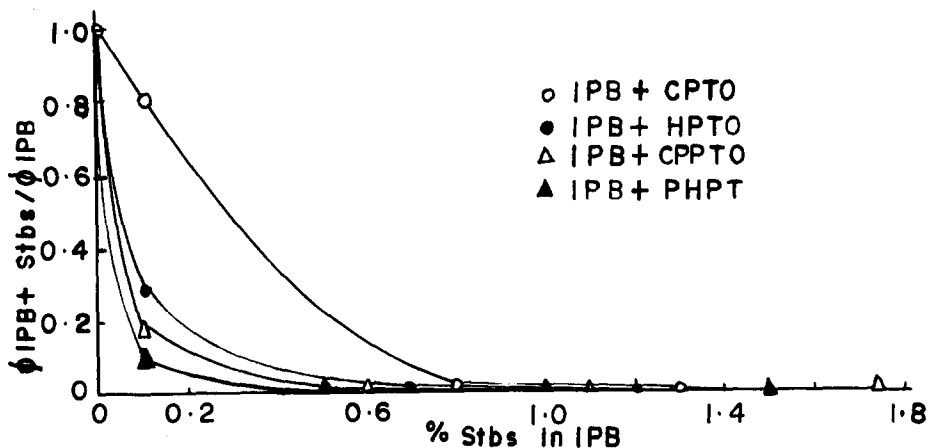


Fig 2. Effect of concentrations of the stabilizers on the ratio of quantum yield of IPB at 283 K.

TABLE 1

Quantum yields of poly(1-butene) chain scissions in the absence and presence of the different stabilizers at various temperatures.

Light intensity flux : 2.38×10^{-9} Einstein sec.⁻¹ cm.⁻²

Irradiation wavelength (λ) : 253.7 nm

Temp. oK	IPB + 0.1% CPTO		IPB+0.1% HPTO		IPB + 0.1% CPPTO		IPB+0.1% -PHPT		
	IPB $\phi \times 10^3$ chain scissions per absorbed photon	ϕ (IPB) ϕ (IPB+CPTO) $\phi \times 10^3$ chain scissions per absorbed photon	IPB $\phi \times 10^3$ chain scissions per absorbed photon	ϕ (IPB) ϕ (IPB+HPTO) $\phi \times 10^3$ chain scissions per absorbed photon	IPB $\phi \times 10^3$ chain scissions per absorbed photon	ϕ (IPB) ϕ (IPB+CPPTO) $\phi \times 10^3$ chain scissions per absorbed photon	IPB $\phi \times 10^3$ chain scissions per absorbed photon	ϕ (IPB) ϕ (IPB+PHPT) $\phi \times 10^3$ chain scissions per absorbed photon	
267.0	2.364	1.905	0.806	0.651	0.275	0.373	0.158	0.265	0.112
273.0	3.396	3.061	0.901	0.965	0.284	0.578	0.170	0.386	0.114
283.0	5.780	4.698	0.813	1.644	0.284	0.985	0.171	0.658	0.114
293.0	8.226	7.419	0.902	2.591	0.315	1.471	0.179	0.981	0.119
303.0	12.711	11.468	0.902	4.009	0.315	2.480	0.195	1.519	0.120
313.0	18.781	16.949	0.903	6.127	0.326	4.012	0.214	2.460	0.131

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