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Stabilizing Effect of 4-(1-Imidazolyl)-Phenol Against the Oxidation of Polybutadiene by Molecular and Singlet Oxygen

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Introduction

Singlet oxygen $^1O_2(^1\Delta_g)$ is a reactive intermediate in the sensitized photooxidation of several polymers (CARLSSON and WILES,1974,1976; RABEK and RÅNBY,1975,1978; RÅNBY and Rabek,1978),especially polydienes (GOLUB et al,1977,1978; NG and GUILLET,1978; RABEK and RÅNBY,1976,1979a,1979b). It is of commercial interest to determine its role in the deterioration of polymeric materials and to find new effective singlet oxygen quenchers. Various compounds have been reported to quench $^1O_2$ including carotenoids (BELLUS,1978; GARNER and WILLIAMS,1978; FOOTE et al,1970), amines (BELLUS,1978, QUANNES and WILSON,1968) and transition metal chelates (CARLSSON et al,1972,1974; FLOOD et al,1973; ZWEIG and HENDERSON,1975).

This paper presents results of stabilization against the oxidation of cis-1,4-polybutadiene by a new type of singlet oxygen quencher, 4-(1-imidazolyl)-phenol.

Experimental

A commercial sample of cis-1,4-polybutadiene (PB) (Ameripol CB200 from Goodrich Chemical Co.) was purified by dissolving in benzene (analytically pure grade) and precipitating with ethanol (spectral grade) in nitrogen atmosphere. This procedure was repeated twice.

4-(1-imidazolyl)-phenol (IP)(Ega-Chemi,Germany)(chemically pure) was recrystallized twice from n-hexane.

Quenching experiments were performed with rubrene (9,10,11,12-tetra-phenylnaphtacene)(Ega-Chemi,Germany) as the $^1O_2$ receptor. Bleaching of rubrene (RU) absorption at 520 nm was used to follow the rubrene oxidation to endo peroxide. Using visible light (460nm), $^1O_2$ was generated in a solution of benzene and methanol (9:1).Methylene blue (10^{-3}M) was used as photosensitizer(RABEK and RÅNBY,1976,1979a,1979b).

The stabilization effect of IP for the UV(254 nm) photodegradation of PB in benzene solution (1 wt-%) was measured by determining the amount of chain scission (S). This chain scission,where $S = (M_{vo}/M_{vt}-1)$,was estimated from viscometric measurements of 1,4-PB solution in benzene at 32°C using an Ubbelhode viscometer. The effects of IP were compared with those of 2,6-di-tert-butyl-p-cresol (DTBC)(Ega-Chemi,Germany) which is an active free radical scavenger. The stabilization

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effect of IP on $^1O_2$ oxidative degradation of PB in benzene-methanol (9:1) solution was determined by measuring S with and without IP and was compared with β-carothene (Eastman Kodak).

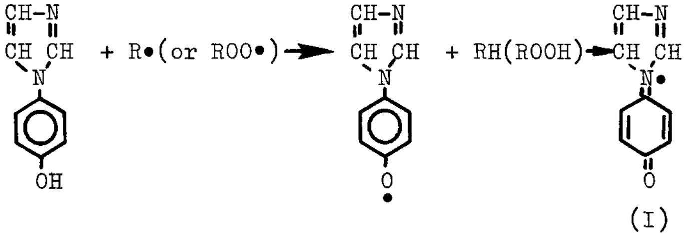
The visible light source was a Philips tungsten lamp (500 W) with an additional filter (OG515 Schott) cutting off light below 515 nm. A low-pressure mercury lamp,type Philips 125 W, generating 254 nm radiation,was used as the UV light source.

The electron spin resonance (ESR) spectra were determined with a Bruker ESR spectrometer using accesories for liquid samples and low temperatures. The measurements were limited to a study of free radicals formed at 77K from IP at a concentration of 10^{-2} M in methanol using 254 nm radiation. A more detailed study of the free radicals formed will be presented in a separate paper.

Results and discussions

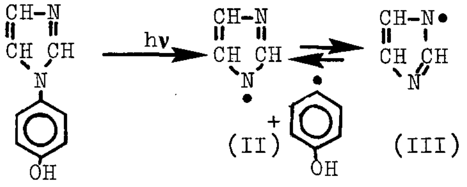
The study of the stabilizing effect of 4-(1-imidazolyl)-phenol (IP) was made for two cases:

1. Stabilization against photodegradation of PB by UV light (254 nm) in the presence of oxygen. The stabilization of PB occurs as a free radical mechanism with the formation of quinoid-imidazole radicals:



(1)

A similar mechanism of stabilization by substituted phenols has been proposed previously (RABEK,1975,RÅNBY and RABEK 1975). In this case we observed that IP is a much more effective stabilizer than DTBC (Fig.1). Irradiation at 254 nm decomposes IP easily (Fig.2) into free radicals (Fig.3). The main ESR spectrum observed during UV irradiation in both oxygen-free atmosphere and in the presence of oxygen is a triplet spectrum with a hyperfine splitting constant H=18 G (Fig.3). This spectrum can be attributed to the unpaired electron at the N atom. This type of free radical can arise from cleavage of the bond between the imidazole ring and the phenol groups (E_{C-N} = 72.8 kcal/mol). Further rearrangement could also occur:



(2)

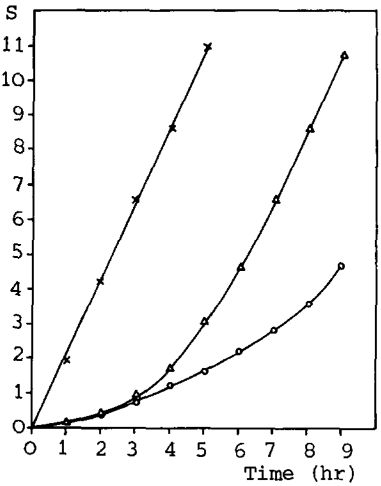


Fig.1 Chain scission (S) of PB as a function of UV(254 nm) irradiation time:
(x) pure PB; (▲) with DTBC (10^{-3}M);(o)with IP(10^{-3}M).

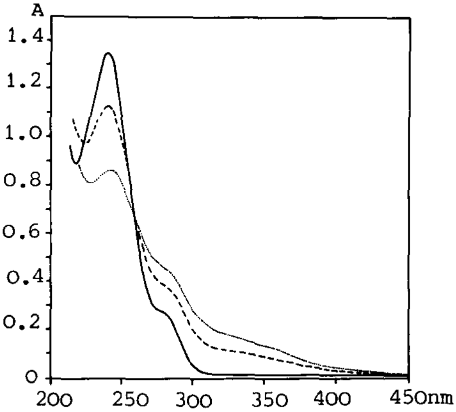


Fig.2 Absorption spectra of IP in CH_3OH (10^{-4}M);
(——) before irradiation;
(- -) after 15 min UV(254 nm)irradiation;
(·····) after 30 min UV(254 nm)irradiation.

The triplet line spectrum is superimposed by a signal from another type of radical which is difficult to identify at present. A more detailed study of the ESR spectra of this radical is being continued. Free radicals (II) and (III) may also participate in the photostabilization of PB by reaction with polymer radicals and polymer peroxy radicals.

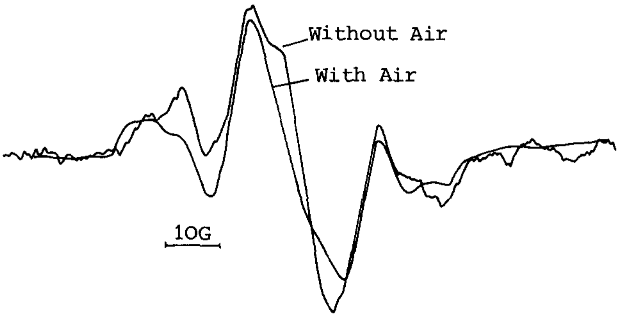


Fig.3. ESR spectra of IP(10^{-2}M) in CH_3OH (at 77 K) after 20 min UV (254 nm) irradiation.

2. Stabilization against $^1O_2$ oxidation of PB. In this case we observed that IP is a less effective stabilizer against $^1O_2$ than β-carothene (Fig.4). In order to calculate the quenching rate constant, k_q, for IP, rubrene (RU) was used since it can generate $^1O_2$ photochemically and can simultaneously act as $^1O_2$ acceptor. The following reactions were taken into consideration:

$$RU + h\nu \longrightarrow RU^* \qquad (3)$$

$$RU^* + {}^3O_2 \longrightarrow RU + {}^1O_2 \quad (R_i) \qquad (4)$$

where: R_i is the rate of $^1O_2$ formation.

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \qquad (5)$$

$$RU + {}^1O_2 \xrightarrow{k_{ox}} RUO_2 \qquad (6)$$

$$IP + {}^1O_2 \xrightarrow{k_q} IPO_2 \text{ (or } IP + {}^3O_2) \qquad (7)$$

The rate of bleaching of RU in the absence of IP is given by:

$$-\left(\frac{d[RU]}{dt}\right)_1 = \frac{R_i\ k_{ox}\ [RU]}{k_{ox}\ [RU] + k_d} \qquad (8)$$

The rate of bleaching of RU in the presence of IP is given by:

$$-\left(\frac{d[RU]}{dt}\right)_2 = \frac{R_i\ k_{ox}\ [RU]}{k_{ox}\ [RU] + k_d + k_q\ [IP]} \qquad (9)$$

Dividing eq.(8) by eq.(9) we obtained:

$$\frac{(d[RU]/dt)_1}{(d[RU]/dt)_2} = 1 + \frac{k_q\ [IP]}{k_{ox}[RU] + k_d} \qquad (10)$$

The quenching rate constant (k_q) for IP can then be obtained directly from eq.(10):

$$k_q = \frac{k_{ox}\ [RU]\ +\ k_d}{[IP]} \cdot \left(\frac{(d[RU]/dt)_1}{(d[RU]/dt)_2} - 1\right) \qquad (11)$$

The values $k_{ox}=1.7x10^8 M^{-1}s^{-1}$ (in toluene) and $k_d=10^5 M^{-1}s^{-1}$ were obtained from (FOOTE et al,1970). Bleaching curves of RU in the presence of IP are shown in Fig.5. The rate constant (k_q) for IP (in toluene) calculated from these results is $k_q=1.94x10^8 M^{-1}s^{-1}$. This value is much lower than the rate constant (k_q) for β-carothene, $3x10^{10} M^{-1}s^{-1}$ (in toluene) (ZWEIG and HENDERSON,1975). The mechanism of $^1O_2$ quenching by IP is not yet well understood. The deactivation of $^1O_2$ can involve either a route whereby the IP undergoes no ultimate chemical change (physical quenching) or one involving a chemical reaction which results in a new product. The quenching ability of IP for $^1O_2$ of the same order as thiobisphenolate nickel chelate stabilizers (ZWEIG and HENDERSON,1975) which act both as antioxidants and as $^1O_2$ quenchers and are used commercially. IP appears to be a promising stabilizer against $^1O_2$ and simultaneously against free radical oxidation.

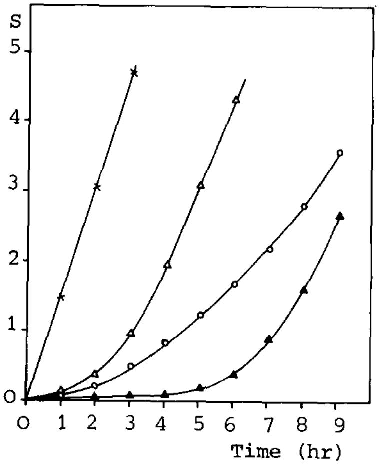


Fig.4. Chain scission (S) of PB as a function of visible (> 460 nm) irrad. with methylene blue (10^{-3}M) in benzene-methanol (9:1) solution: (x) pure PB; (Δ) PB + β-carothene (10^{-4} M); (○) PB + IP (10^{-3}M); (▲) PB + β-carothene (10^{-3} M).

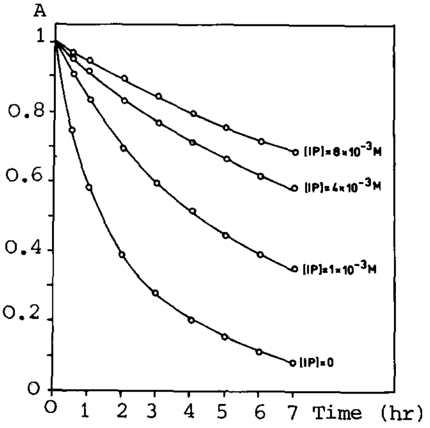


Fig.5.Rubrene photooxidation in toluene (10^{-4}M) in the presence of different concentrations of IP.

Acknowledgment

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