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Photosensitization and Photostabilization of Isotactic Poly(1-Butene) Film with Triazine Complexes

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ABSTRACT

This work describes the results of the 3-(o-carboxyphenyl)-1-phenyltriazine-N-oxide [CPT] -sensitized and copper(II) bis-3-(o-carboxyphenyl)-1-phenyltriazine-N-oxide [CCPT] - stabilized photodegradation of isotactic poly(1-butene) film in air at a temperature range of 267-313°K with a light intensity flux 2.38×10^{-9} einsteins $sec^{-1}cm^{-2}$. The degradation was followed by viscometry, potassium ferri-oxalate actinometry and by measuring carbonyl index. The intrinsic viscosity, quantum yield and carbonyl index depend on several factors, i.e., temperature and triazene concentration.

INTRODUCTION

The present knowledge of stabilization and sensitization of polymers can be conveniently called in its 'initial stage'. However, the wide-spread usage of these polymeric materials in industry, military, space technology and house-hold articles, require their sensitization and protection against solar irradiation. Many applications require these materials with high resistance to light, natural and induced environmental attack whereas other applications require the production of such materials which end up in some form of garbage-disposal system.

In the present work, therefore, evidence concerning the kinetics by which 3-(o-carboxyphenyl)-1-phenyltriazene-N-oxide and copper(II) bis-3-(o-carboxyphenyl)-1-phenyltriazene-N-oxide sensitized and stabilized poly(1-butene) has been described. The effect of these chelates has been obtained by studying the variation in intrinsic viscosity [η], quantum yield [ϕ_{cs}] and carbonyl index during the photooxidative degradation of poly(1-butene) film with 254 nm light at temperature from 267 to 313°K where volatile formation is negligible. CCPT behaved as oxidation retarder whereas CPT merely enhanced oxidation and the effects of both triazene increased correspondingly with increasing concentration.

EXPERIMENTAL

By the courtesy of Mobil Chemical Co., Metuchem, New Jersey,USA, isotactic poly(1-butene) [IPB] was obtained and the atactic portion of it was removed according to the procedure of NATTA et al. (1956). The polymer sample was washed with ether (40-60°C) and dried in vacuo. The ligand, 3-(o-carboxyphenyl)-1-phenyltriazene-N-oxide [CPT] was synthesized with the literature procedure of MAJUMDAR (1968) by coupling the diazotized anthranilic acid with freshly prepared phenylhydroxylamine. For the synthesis of copper(II) bis-3-(o-carboxyphenyl)-1-phenyltriazene-N-oxide [CCPT] , cupric chloride was coupled with 3-(o-carboxyphenyl)-1-phenyltriazene-N-oxide. CHANDRA et al. (1980a) have described the method of film preparation, irradiation and incorporation of the stabilizer in the film matrix. The irradiated films with and without the stabilizer were dissolved in cyclohexane. Ubbelohde viscometer was employed for viscosity measurement at 35.0 ± 0.05°C. Flow solutions were separately pipetted out into the viscometer and sufficient time is given for thermal equilibrium. For cyclohexane solvent and for IPB film solution, flow-times were determined separately. Flow-times of film solutions were determined at five different concentrations. The quantum yields for photo-oxidative degradation and stabilization were determined with potassium ferrioxalate actinometer.

RESULTS AND DISCUSSION

The intrinsic viscosities $[\eta]$ of the irradiated IPB films in the absence and presence of 0.1 wt.-% CPT and 0.1 wt.-% CCPT in the temperature range of 267 to 313°K in air were determined by extrapolating reduced viscosities to zero concentration.

Intrinsic viscosities $[\eta]$ of irradiated films with a light intensity flux of 2.38×10^{-9} einsteins $sec^{-1}cm^{-2}$ with different time intervals in the absence and presence of CPT and CCPT in air at 283°K have been summarized in Table 1. The table shows

TABLE 1. Intrinsic viscosities $[\eta]_t$ in dl g^{-1} for photo-oxidative degradation and stabilization of IPB in the absence and presence of 0.1 wt.-% CPT and 0.1 wt.-% CCPT in air at 283°K.
Light intensity flux = 2.38×10^{-9} einsteins $sec^{-1}cm^{-2}$. Irradiation wavelength (λ) = 253.7 nm.

Time of irradiation (hrs)	IPB $[\eta]_t$	IPB + CPT $[\eta]_t$	IPB + CCPT $[\eta]_t$
0.0	5.11	5.11	5.11
2.0	5.03	5.01	5.07
4.0	4.96	4.93	5.04
6.0	4.89	4.86	5.02
8.0	4.86	4.81	4.99
10.0	4.82	4.79	4.96
12.0	4.81	4.77	4.97
14.0	4.80	4.77	4.99

a rapid decrease in $[\eta]_t$ initially which then slows down and the decrease of $[\eta]_t$ is larger of the irradiated film with CPT and lesser with CCPT as compared with the corresponding values of the base films. This indicates that CPT enhances whereas CCPT retards the photo-oxidative degradation of IPB. JELLINEK et al. (1970) and CAMERON et al. (1982) have contended that initial change in $[\eta]_t$ is due to the scission of weak bonds by the attack of oxygen. The increase in $[\eta]_t$ at longer irradiations suggests that crosslinking predominates at longer exposures.

DAN et al.'s (1973) equation was used to calculate the quantum yields for chain scission:

$$\phi_{cs} = \frac{\left[\left([\eta]_o \,/\, [\eta]_t \right)^{1/\alpha} - 1\right] m}{\bar{M}_{no}\ I} \qquad (1)$$

where ϕ_{cs} is the quantum yield, $[\eta]_o$ and $[\eta]_t$ are the intrinsic viscosities of the unirradiated and irradiated films, respectively; α is the viscosity expansion factor, m is the weight of irradiated film, M_{no} is the number-average weight of the polymer before irradiation and I is the intensity of the irradiation in einsteins.

The viscosity-average molecular weight M_{no} of irradiated IPB films in the absence and presence of CPT and CCPT in cyclohexane were calculated from the experimentally determined value of $[\eta]$ at 35 ± 0.05°C using the well known Mark-Houwink relationship:

$$[\eta]\ (\mathrm{dl/g}) = 2.94 \times 10^{-4}\ M_v^{-0.69} \qquad (2)$$

BAMFORD et al. (1958) have converted $\bar{M}_v$ to $\bar{M}_n$ by the equation:

$$\frac{\bar{M}_v}{\bar{M}_n} = \left[\frac{\Gamma(3 + a)}{2^{(1 + a)}}\right]^{1/a} \qquad (3)$$

where $\Gamma(3 + a)$ is the gamma function of $(3 + a)$ and a is the exponent in Mark-Houwink's relationship.

The plots of quantum yields in the absence and presence of CPT and CCPT as a function of temperature are shown in Figure 1. The increase in quantum yield with temperature is probably due to the increased mobility of the polymer chain at higher temperature. The higher quantum yields are with CPT at all temperatures whereas lowers are in the presence of CCPT in comparison

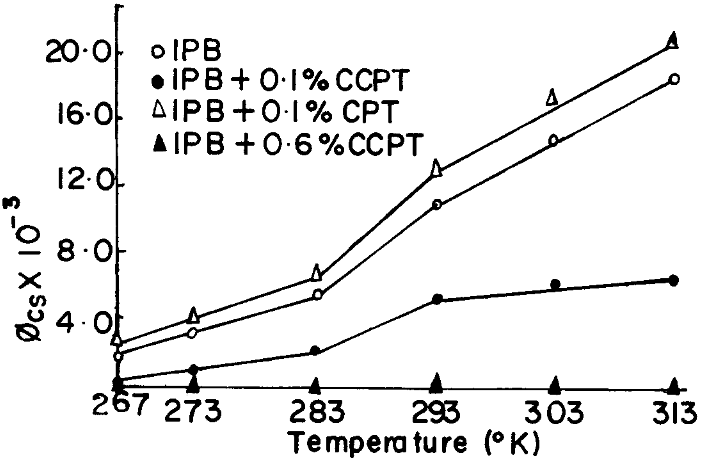

FIG. 1. Quantum yield for photodegradation and stabilization of IPB in the absence and presence of stabilizer vs. temperature

of base IPB. A saturation limit in photostabilization is achieved at 0.6 wt.-% CCPT in IPB. It is clear from the figure that CPT enhances the degradation whereas CCPT retards it.

The photo-oxidative degradation rate was measured by means of a carbonyl index at 1721 cm^{-1} using a Perkin-Elmer (Model 21) infrared spectrophotometer:

$$\text{Carbonyl index} = \left[(\log I_o/I_t)/d\right] \times 100 \qquad (4)$$

where I_o is the intensity of incident light, I_t is the transmitted light intensity and d is the film thickness in microns. Figure 2 yields the carbonyl index curves vs. irradiation

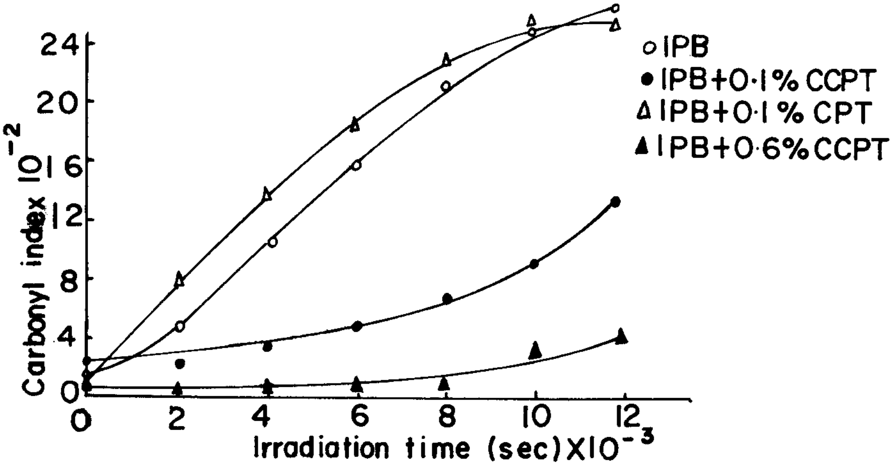

FIG. 2. Carbonyl index for photodegradation and stabilization of IPB in absence and presence of stabilizer at 283°K

times at 283°K. The figure shows that the carbonyl index content of the irradiated film is higher in the presence of CPT and lower in the presence of CCPT as compared to the corresponding values of base IPB.

The CPT has one readily available free carboxy group in its backbone due to which it sensitized the degradation. CCPT stabilizes IPB by interference with the propagation reaction by absorption of UV light. By minimizing the light energy absorbed by the polymer, the primary photochemical processes are prevented. In addition to this the CCPT inhibits the initiation process by electron transfer and formation of charge-transfer inert complex.

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