J. Braz. Chem. Soc., Vol. 18, No. 5, 900-910, 2007.
Printed in Brazil - ©2007 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Effects of Bismuth Vandate and Anthraquinone Dye on the Photodegradation of Polycarbonate

Clodoaldo Saron,[a] Maria Isabel Felisberti,*,[a] Fabio Zulli[b] and Marco Giordano[b]

[a]*Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13084-971 Campinas-SP, Brazil*

[b]*Dipartimento di Fisica 'Enrico Fermi', Università di Pisa and polyLab*
Largo Bruno Pontecorvo 3, I-56127 Pisa, Italy

Compostos orgânicos e inorgânicos, tais como óxidos, sais de metais, compostos policíclicos e azo, são freqüentemente usados como colorantes para polímeros. O pigmento vanadato de bismuto vem sendo usado como uma alternativa a pigmentos baseados em cádmio. Corantes baseados na antraquinona pertencem a classe de colorantes policíclicos amplamente usados em polímeros. Além de suas características como colorantes, o vanadato de bismuto e colorantes a base de antraquinona apresentam atividade fotocatalítica ou propriedades fotoquímicas que podem influenciar o mecanismo e a cinética de fotodegradação do polímero que o contem. Neste trabalho estudou-se a influencia do pigmento vanadato de bismuto e de um corante a base de antraquinona sobre a fotodegradação do policarbonato. Para tanto, amostras de policarbonato contendo os colorantes foram submetidas a envelhecimento fotoquímico de acordo com as recomendações da ASTM G53. Os resultados indicaram que o vanadato de bismuto acelera a fotodegradação do policarbonato, causando uma acentuada perda nas propriedades mecânicas e aumento na concentração de hidroperóxido durante o envelhecimento. As características relacionadas a cor do pigmento também foram alteradas. O comportamento do policarbonato contendo o vanadato de bismuto frente a fotodegradação é atribuído a possíveis reações envolvendo o polímero e o pigmento promovidas pela radiação UV. Por outro lado, a presença de um corante a base de antraquinona aparentemente estabilizou o policarbonato frente à fotodegradação através de um mecanismo de desativação de estados excitados no policarbonato.

Both inorganic and organic compounds, such as oxides or salts of metals and polycyclic and azo compounds, are frequently used as colorants in polymeric systems. Bismuth vanadate pigment has been used as an environmentally friendly alternative for cadmium containing pigments and anthraquinone dyes represent a polycyclic colorant class of wide use in polymers. Besides their coloring properties, both bismuth vanadate and anthraquinone present photocatalytic activity or photochemical properties that can influence the mechanism and the kinetics of the photodegradation of the polymer into which they are incorporated. In this paper the influence of bismuth vanadate pigment and anthraquinone dye on the photodegradation of polycarbonate was evaluated. For this purpose, samples of polycarbonate containing the colorants were submitted to photochemical aging following the recommendations of ASTM G53. Bismuth vanadate accelerates the photodegradation of polycarbonate, causing a faster drop in the mechanical properties and an increase in the hydroperoxide concentration during the aging process. The coloring ability of the pigment is also affected. The photodegradation behavior of polycarbonate in presence of bismuth vanadate may be caused by a possible direct chemical reaction between pigment and polymer, promoted by UV radiation. On the other hand, the presence of anthraquinone dye seems to stabilize the polycarbonate against photodegradation through a deactivation mechanism of the excited state.

Keywords: photodegradation, colorant, polycarbonate, bismuth vanadate pigmentm anthraquinone dye

---

*e-mail: misabel@iqm.unicamp.br

Introduction

A number of organic and inorganic compounds absorb light in the visible portion of the electromagnetic spectra and, because of this, they are colored. However, few colored compounds can be used as colorants in polymeric systems. Among other properties, polymeric colorants should be chemically compatible with the polymer and stable to the thermal and mechanical conditions normally used during polymer processing. The main polymeric colorants are classified into azo, polycyclic, metal oxides and metallic salts as well as organic-inorganic complexes.[1-5]

Bismuth vanadate ($BiVO_4$) is an yellow pigment widely used in ceramics and polymeric systems. $BiVO_4$ is usually obtained by solid-state reactions, in which stoichiometric quantities of Bi and V containing precursors are mechanically mixed and heated to approximately 700 ºC in air or another oxidizing atmosphere. Due to the toxicity of the main yellow pigments, such as that containing cadmium, the interest in searching for alternatives has grown. Among them $BiVO_4$ has been considered as very interesting.[6,7]

Other properties of $BiVO_4$ such as ferroelasticity and ion conduction have also attracted attention. These properties are strongly dependent on the crystal structure, which can be the tetragonal zircon structure, the monoclinic scheelite structure or the tetragonal scheelite structure.[8] Under heat treatment, reversible and irreversible phase transitions between these crystal structures occur. The changes in the ferroelastic properties through the phase transitions have been widely studied. At temperatures above 600 ºC, monoclinic structure formation occurs. Monoclinic $BiVO_4$ has shown high activity in photocatalytic O_2 evolution under light irradiation. The activity of monoclinic $BiVO_3$ has been found to be much higher than that of commercial WO_3, which is a well-known photocatalyst for the O_2 evolution reaction under visible light irradiation. This is due to the smaller band gap of monoclinic $BiVO_4$ and its high quantum yield.[8-12]

On the other hand, anthraquinone dyes are polycyclic colorants frequently used in polymer and in the textile and photographic industries. These kinds of compounds play an important role, not only as dyestuffs, but also in biological systems or in functional materials such as organic photoconductors. The properties of anthraquinone dyes such as color, solubility and reactivity are strongly dependent on their chemical structures. It is known that some anthraquinones exhibit interesting photochemical and photophysical properties.[13-16] For 1,4-anthraquinone an intersystem crossing $S_1(n, \pi^*) \rightarrow T_1(\pi, \pi^*)$ is expected to predominate. Thus, the observed emission for such a system is normally only phosphorescence from $T_1(\pi, \pi^*)$.[13] Itoh *et al.*[13] have reported that 1,4-anthraquinone exhibits the dual fluorescence from the $S_2(\pi, \pi^*)$ and $S_1(n, \pi^*)$ states in a fluid solution at room temperature, beside the phosphorescence from the $T_1(\pi, \pi^*)$ state in rigid glass at 77 K.

The features of anthraquinone dyes and bismuth vanadate lead to unexpected results in photodegradation processes involving polymeric systems containing these colorants, which can not be foreseen without practical experiments. In the present work, the action of the anthraquinone dye and the bismuth vanadate pigment on the photodegradation of polycarbonate has been investigated.

There are a number of studies on the photodegradation of polycarbonate using ultraviolet radiation, which can be grouped into methods utilizing photolysis with shorter wavelengths (< 300 nm), and photolysis with longer wavelengths (> 300 nm).[17-20] For photodegradation at shorter wavelengths, the mechanism is characterized by Photo-Fries reactions: a direct bond scission, initiated at the carbonate linkage, leads to the formation of free radicals.[19] Further cross-linking of these free radicals leads to the formation of phenyl salicylates, dihydroxybenzophenones, dihydroxybiphenyl etc. With longer wavelengths, polycarbonate photodegradation occurs by a photooxidation mechanism involving reactions in side chain, formation of quinone groups in the aromatic rings and the opening of aromatic rings.[20]

Experimental

Samples

Polycarbonate (in powder form) was obtained from GE Plastics South America. The $BiVO_4$ pigment (Irgacolor 2GTM®), the anthraquinone dye (Oracet GHS®), the free radical probe (Tinuvin 770®), and a secondary processing antioxidant (Irgafos 168®) were obtained from CIBA Specialty Chemicals.

The colorants and the Irgafos 168 were incorporated into the polycarbonate at 1% m/m and 0.15% m/m, respectively, during an extrusion molding process in a simple screw extruder, Wortex® L/D 32, with a Madock mixer element. Polycarbonate containing only Irgafos 168 was also prepared. Samples for stress-strain tests (ASTM D 638) were prepared by the injection molding process in an Arburg Allrounder 221 KS 9250-75) equipment. The following conditions were used: temperature range of 160 °C to 300 °C; mold temperature of 90 °C; pressure of 750 bar.

Accelerated photochemical aging

Specimens for stress-strain tests of polycarbonate and polycarbonate containing bismuth vanadate pigment and anthraquinone dye were submitted to different photochemical aging times in an equipment manufactured according to suggestions of ASTM G-53 Standard Practice for UVA radiation.[21] UVA radiation (315-400 nm) was produced by a set of Philips model CLEO Performance 80W-R mercury lamps. Cycles of radiation at room temperature and water condensation in the specimen region were performed, following the procedure: 22 h of radiation exposure (25-30 °C), followed by 2 h of condensation cycle (around 50 °C). Only one face of the samples was irradiated.

Spectroscopic analysis

UV/Visible absorption spectra of anthraquinone dye were obtained in hexane solution, using a Hewlett Packard 8456 A spectrometer. Reflection spectra of bismuth vanadate were obtained by spectra subtraction of specimens for stress-strain tests of polycarbonate containing bismuth vanadate and polycarbonate without colorant, using a Macbeth Color-eye spectrometer.

Mechanical testing

Stress-strain tests were performed on an EMIC LA2000 universal machine at a low strain rate (6 mm min^{-1}). Before the measurements, the specimens were kept at 25 °C and 50% humidity for 48 h. At least six specimens were tested. The material performance as a function of the aging time was evaluated by the mechanical property of elongation at break.

Hydroperoxide analysis

Hydroperoxide analysis was carried out using a standard iodometric method.[22,23] Aged specimens of polycarbonate and polycarbonate containing bismuth vanadate pigment and anthraquinone dye were cut into small cubic-shaped pieces (0.5 g) and placed into round-bottomed flasks with glacial acetic acid (0.5 mL), isopropanol (9.5 mL) and a small amount of sodium iodide. The mixture were refluxed for 30 min, then cooled in an ice bath and filtered through filter paper. Blank solutions ware also prepared, using not aged specimens. Immediately after preparation, the UV-Vis absorbance of each solution was measured at 420 nm in a Hewlett Packard 8453 A-Diode Array spectrometer. The hydroperoxide concentration was determined from an analytical curve prepared using hydrogen peroxide.

Scanning Electron Microscopy (SEM)

SEM images of the aged surface of specimens were also acquired. The samples were fixed in a metallic support and covered with carbon. The analyses were performed with a JEOL L360-LV at 60º to the detector.

Colorimetry

Color changes of the aged specimens were monitored by the ΔE parameter, which is calculated by the square root of the square of the coordinates L*, a*, b* (color parameters), according to the CIELAB color system, following the procedures of ISO 7724 Standard Practice. The analyses were conduced using a Macbeth Color-eye spectrometer, in the reflection mode with illuminant D.

Electron Spin Resonance (ESR)

ESR measurements were carried out with a Bruker ER 200D SRC X-band spectrometer (microwave frequency about 9.5 GHz), equipped with a Bruker ER035M NMR gauss-meter. In order to improve the signal to noise ratio a phase revelation of the signal is performed by modulating the magnetic field. Due to the amplitude modulation of the magnetic field, ESR line-shapes are obtained in their first derivative form. Quartz tubes were used to hold the samples in the cavity of the spectrometer.

The ability of bismuth vanadate, anthraquinone dye and polycarbonate to generate reactive chemical species under UVA radiation was tested using the following procedure: the probe bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (Tinuvin 770) was added to the bismuth vanadate, anthraquinone dye, and polycarbonate solutions in $CHCl_3$ (2% m/m). Then the solutions were bubbled with atmospheric air for 20 min and irradiated (0 to 6 h) with same lamp used in the photochemical aging study. Finally, the solutions were submitted to ESR measurements.

Results and Discussion

Spectroscopic analysis

In Figure 1 the reflection and absorption spectra of colorants and the emission spectrum of the lamp used for photochemical aging process are shown.

The emission spectrum of the lamp used in the photochemical aging experiments shows a main emission

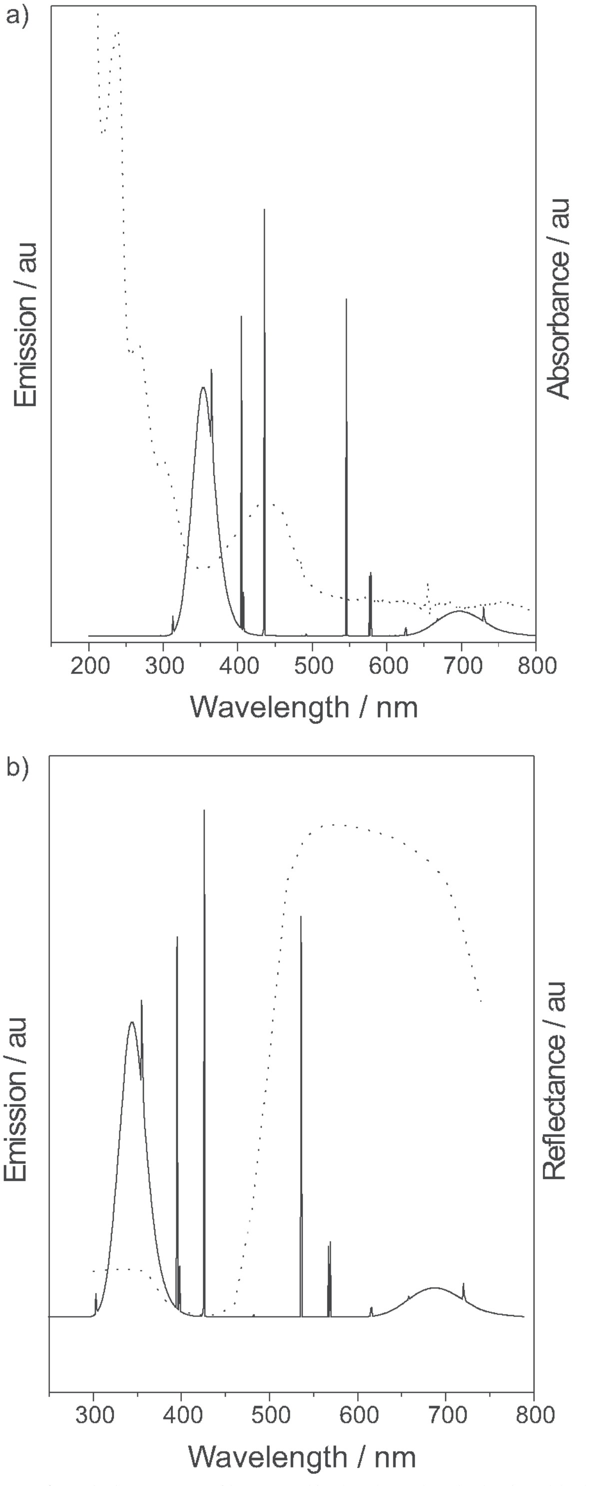


Figure 1. Emission spectra of lamp used in the photochemical aging (black line) and a) absorption spectrum of anthraquinone dye (dotted line), b) reflection spectrum of $BiVO_4$ (dotted line).

band at 315 to 400 nm (UVA). Other emission lines are also verified in the visible region of the spectrum. For the anthraquinone dye (Figure 1a) an absorption band around 450 nm can be observed, which characterizes the orange color presented by the colorant. This absorption band is extended to the ultraviolet spectrum, coinciding with the emission band of lamp. At wavelengths lower than 300 nm, a strong increase in the intensity of the absorption band occurs. Similar behavior is observed for the $BiVO_3$ pigment (Figure 1b), whose reflectance spectrum shows a significant light absorption at 300 to 450 nm. The absorption bands of the anthraquinone dye and the $BiVO_4$ pigment show that these colorants can be excited by the radiation emitted by the lamp.

Elongation at break

The mechanical properties of the polymers are extensively affected by material degradation. Small changes in the physical or chemical structures can cause intense variations in the mechanical properties. Thus, the evaluation of mechanical properties such as elongation at break during the aging process is an important method to evaluate the polymer degradation. Figure 2 shows the behavior of elongation at break of the polycarbonate without additives and when containing the yellow bismuth vanadate pigment and the orange anthraquinone dye as a function of the photoaging time.

For the first hours of aging (of about 228 h) an intense decrease of the elongation at break for polycarbonate containing $BiVO_4$ is observed, while the samples of

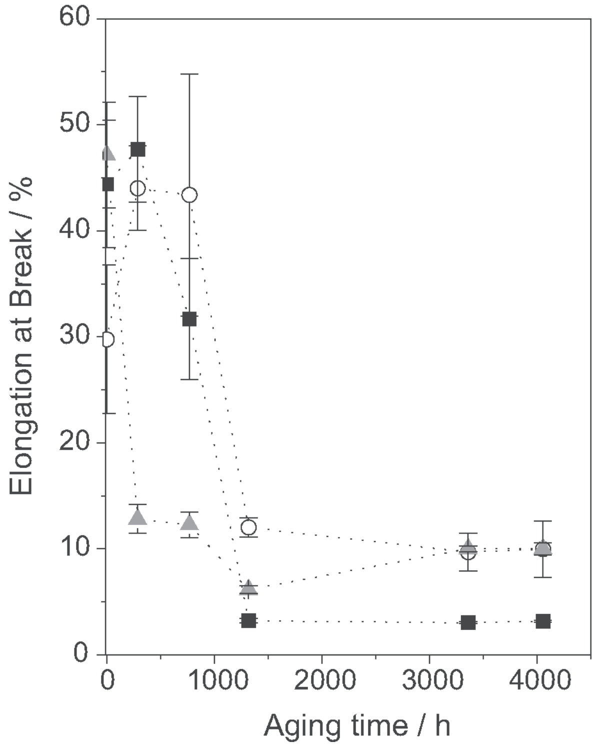


Figure 2. Elongation at break as a function of the aging time: polycarbonate (■), polycarbonate containing anthraquinone (○), and bismuth vanadate (▲).

polycarbonate without additives and the one containing the anthraquinone dye remain practically unchanged in comparison with unexposed polycarbonate. A comparable level of decrease in the elongation at break (~10%) for these latter samples occurs only after 1320 h of aging.

The fast drop in the elongation at break for polycarbonate containing bismuth vanadate pigment suggests that this pigment under ultraviolet radiation produces or catalyzes chemical reactions in the polymer that lead to degradation of the polymer.

Hydroperoxide analysis

Hydroperoxides are generated in polymeric chains during degradation when a free radical formed in the first steps of the degradative process is combined with molecular oxygen.[24] Then, the hydroperoxides are decomposed to two other oxidizing chemical species that lead to a serial chemical reactions and material degradation.[23] Therefore, hydroperoxide determination is a qualitative index indicating if the degradation reactions occur during aging processes. Figure 3 shows the hydroperoxide concentration as a function of the aging time.

Before the aging process, only a residual concentration of hydroperoxide, which can be produced during thermal processing of polymer, is found for polycarbonate either without additives or containing colorants. A small increase of the hydroperoxide content can be observed after 288 h of aging, indicating the beginning of the polycarbonate photodegradation. The hydroperoxide content in the polycarbonate without additives or containing anthraquinone dye remains unchanged after 768 h of aging. However, a significant increase in the hydroperoxide content is verified for polycarbonate containing bismuth vanadate pigment. This is evidence that bismuth vanadate could accelerate the formation of oxidizing reactions when the material is exposed to ultraviolet light.

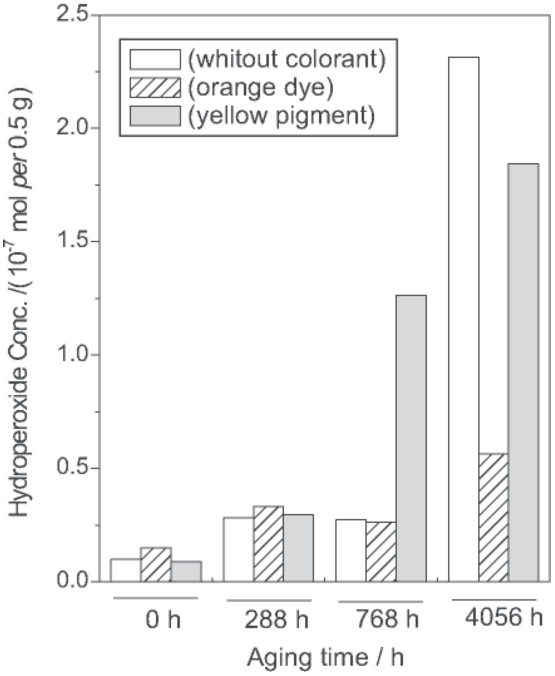


Figure 3. Hydroperoxide content as a function of the aging time.

After 4056 h of aging, when one can consider that hydroperoxide formation and decomposition processes are at equilibrium, the presence of hydroperoxides is more significant for polycarbonate without additives and that containing bismuth vanadate pigment.

Colorimetry

Colorimetric analysis provides important data about color changes in material, which can be related to the formation of the oxidizing groups in the polymeric chains and/or the decomposition of colorants incorporated into polymer. Figure 4 shows the results of the color variation parameter (ΔE) studies during the aging processes.

Intense color variation is observed for polycarbonate without additives and for that containing bismuth vanadate, while polycarbonate containing anthraquinone dye is much less affected.

For the polycarbonate without additives the color variation is caused by formation of quinone groups in the aromatic rings of the polymeric chain.[20] These quinones

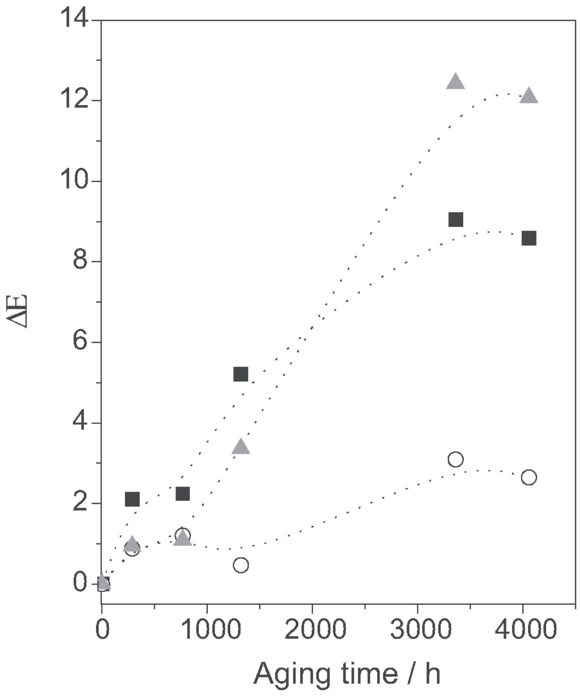


Figure 4. Color variation parameter (ΔE) as a function of aging time for: polycarbonate (■), polycarbonate containing anthraquinone dye (○), and polycarbonate containing bismuth vanadate pigment (▲).

absorb light in the visible portion of the electromagnetic spectra, producing a yellowness in the material.[17] For the polycarbonate containing bismuth vanadate the color variation can also be caused by pigment degradation. It is possible know if the color variation is caused by pigment or by polycarbonate degradation through color coordinates a* and b*. Coordinate a* indicates an increase of the red hue at the long positive axis and green hue at the long negative axis, while coordinate b* indicates an increase of yellow hue at the long positive axis and blue hue at the long negative axis.[25] The color coordinates b* and a* as functions of the aging time are shown in Figures 5 and 6.

A progressive increase in the b* value for polycarbonate without additives during the aging is observed in Figure 5, showing that the color variation ΔE is related to the yellowness of material. On the other hand, for polycarbonate containing bismuth vanadate the b* value, which is initially high (yellow hue), decreases progressively during aging, indicating that color variation in this case is due to pigment degradation. The b* value for polycarbonate containing anthraquinone dye does not show considerable variation during the aging process. The chromatic parameter a* does not change for polycarbonate containing or not anthraquinone dye when the aging time increases (Figure 6), while for polycarbonate containing $BiVO_{4,}$ a* not only changes in magnitude, but also in signal (from negative to positive values).

The initial negative a* value of the polycarbonate containing bismuth vanadate is due to the green hue of the pigment. The change of this parameter with aging suggests its degradation.

Changes of both a* and b* coordinates for polycarbonate containing bismuth vanadate denote pigment degradation. In fact, the approach of a* and b* to the zero value is related to the absence of chromaticity, which is only possible if the pigment has had its chemical structure altered. On the other hand, the small variations of a* and b* value for polycarbonate containing anthraquinone dye indicate that this dye is little affected during the aging process.

Scanning Electronic Microscopy

SEM was used to evaluate the superficial changes of aged polycarbonate without colorants and those containing $BiVO_4$ pigment or anthraquinone dye. The surface of the material is exposed to more severe degradation conditions during photochemical aging with respect to the bulk, due to direct ultraviolet light incidence and to the presence of oxygen and moisture. The changes in the surface of the material directly affect some quantities such as mechanical properties and light reflection. Figure 7 shows SEM images of polycarbonate before aging and after 3360 h of aging.

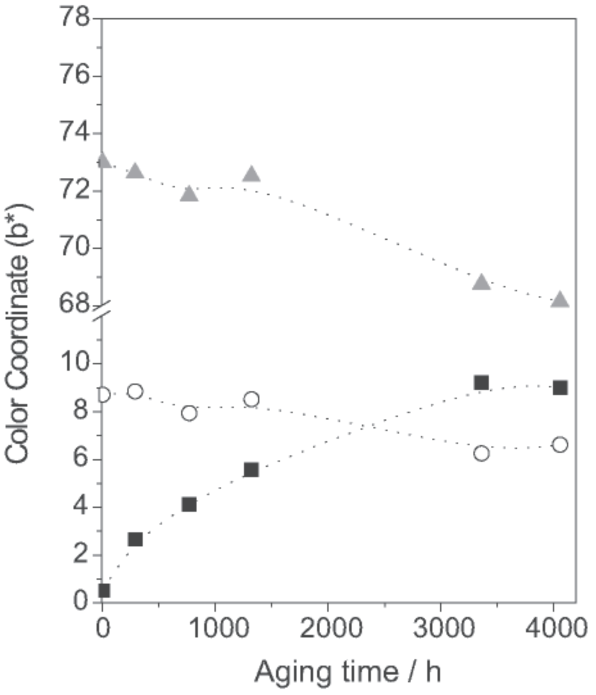


Figure 5. Chromatic parameter b* as a function of aging time for: polycarbonate (■), polycarbonate containing anthraquinone dye (○), and polycarbonate containing bismuth vanadate pigment (▲).

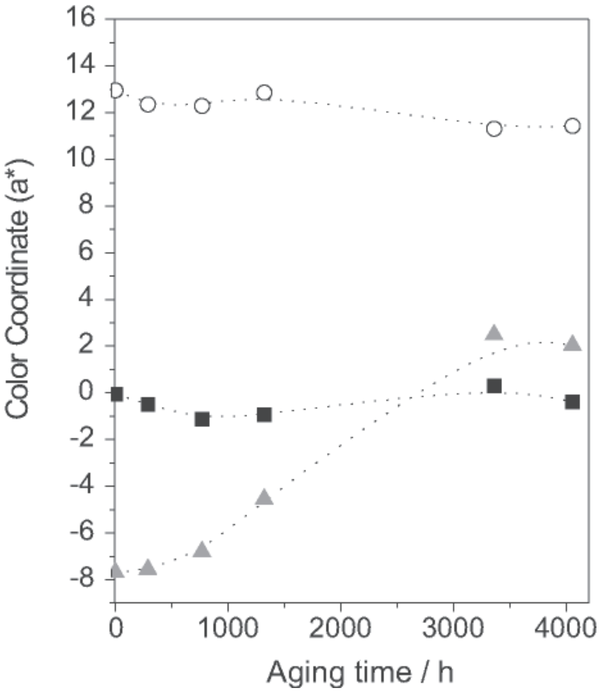


Figure 6. Chromatic parameter a* as function of aging time for: polycarbonate (■), polycarbonate containing anthraquinone dye (○), and polycarbonate containing bismuth vanadate pigment (▲).

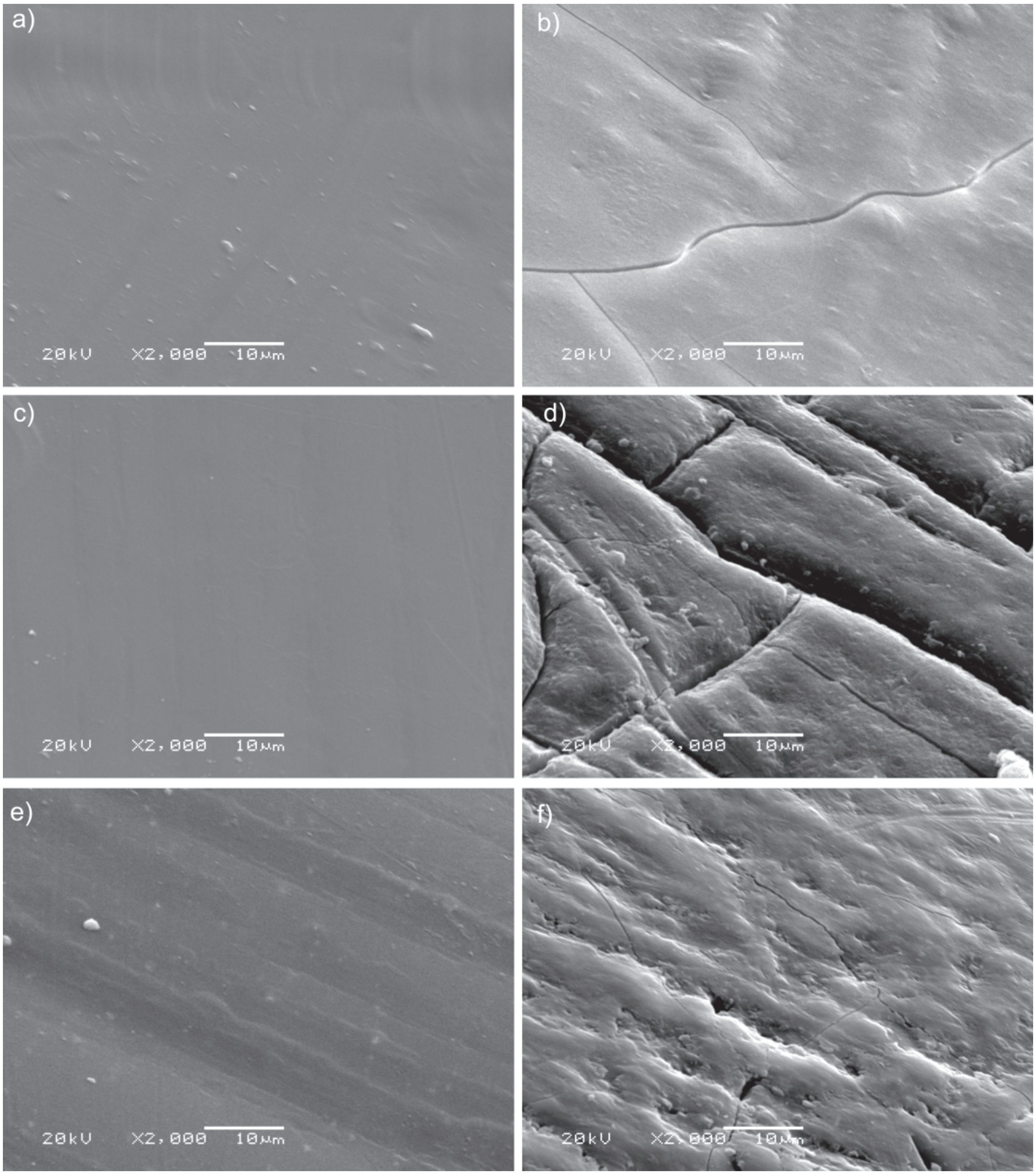


Figure 7. Scanning electron photomicrographs: polycarbonate (a) before and (b) after 3360 h of aging, polycarbonate containing anthraquinone dye (c) before and (d) after 3360 h of photochemical aging, polycarbonate containing bismuth vanadate (e) before and (f) after 3360 h of photochemical aging.

Before the aging process no superficial irregularity was verified for polycarbonate without colorants or containing anthraquinone dye. For polycarbonate containing $BiVO_4$ some points having different contrasts distributed throughout surface can be observed. These spots can be aggregates of pigment particles that were not fully dispersed during polymer processing.

After 3360 h of photochemical aging intense changes occur in the polycarbonate surface. For polycarbonate without colorants the surface shows the formation of cracks that span the entire surface. A similar crack formation occurs for aged polycarbonate containing anthraquinone dye. However, for aged polycarbonate containing $BiVO_4$ the crack formation is less significant while other superficial deformations can be observed such as voids, sinks and cavities. These superficial deformations are similarly distributed as the points of contrast in the non-aged samples and can be caused by matrix corrosion around aggregates of the pigment due to a photocatalytic action of the pigment under polycarbonate degradation when the material is exposed to the aging conditions.

Electronic Spin Resonance (ESR)

ESR is sensitive to paramagnetic species such as free radicals and ions of the transition metals and is frequently used to detail mechanisms and interactions between chemical species in chemical reactions. These ESR features were used to improve understanding of the action of $BiVO_4$ pigment and anthraquinone dye in polycarbonate photodegradation.

Evaluation of the ability of $BiVO_4$ pigment and anthraquinone dye to produce oxidative species in the presence or absence of polycarbonate was carried out by ESR using the probe bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (Tinuvin 770). The Tinuvin 770 is used as a photostabilizer for many polymers, belonging to the photostabilizer group of hindered amine light stabilizers (HALS).[26] Tinuvin 770 is sensitive to attacks of oxidative species such as oxygen singlet or radicalar chemical species generated in the system during the photochemical process, which are the precursors of polymer degradation. The reaction of the oxidative species with Tinuvin 770 produces a stable free radical (Figure 8) that shows an ESR signal.[27,28]

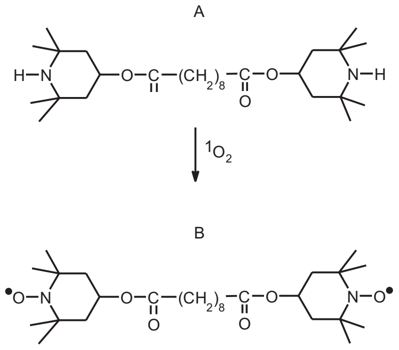


Figure 8. Molecular conversion of Tinuvin 770 to radicalar form.

Many free radicals cannot be easily detected because they are normally unstable, presenting short lifetimes. Tinuvin 770 (form A) does not show an ESR signal before the oxidative reaction occurs. On the other hand, an intense signal appears when Tinuvin 770 is oxidized, forming the stable free radical piperidinoxyl (form B). Thus, the intensity of the piperidinoxyl ESR signal is a function of the formation of other unstable free radicals generated in the system, that transfer the unpaired electron to Tinuvin 770, or of the action of oxidative chemical species than can directly convert Tinuvin 770 from form A to form B.[27,28]

Figure 9 shows sequential ESR of a Tinuvin 770 solution in $CHCl_3$ in the absence and the presence of polycarbonate, obtained immediately after exposition to UV radiation produced by the same lamp used in the photochemical aging experiments.

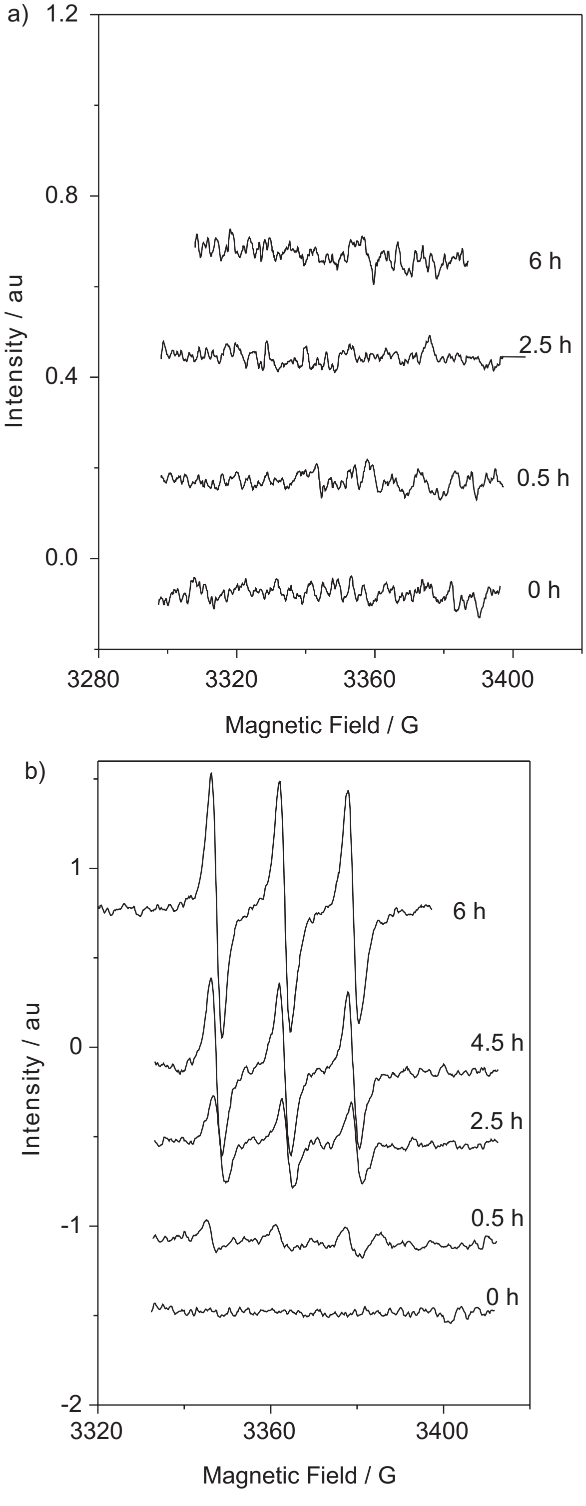
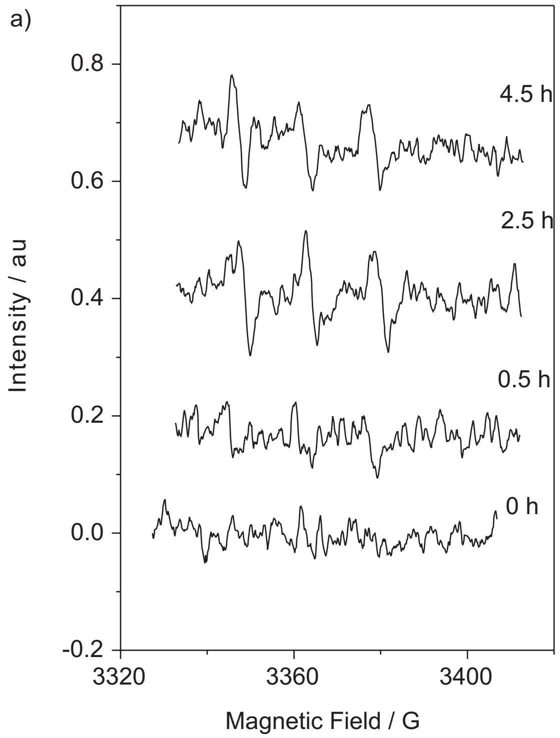


Figure 9. ESR spectra of Tinuvin 770 solutions after UV irradiation: a) without colorants or polycarbonate, b) in presence of polycarbonate.

No characteristic signal is observed in the ESR spectra of the Tinuvin 770 solution when it is exposed up to six hours of irradiation (Figure 9a). However, a three-line signal characteristic of oxidized Tinuvin 770 (piperidinoxyl structure) appears with a progressive increase in intensity during exposition when polycarbonate is added to the Tinuvin 770 solution (Figure 9b). This signal might be caused by the formation of unstable free radicals in the polymeric chains of polycarbonate after hydrogen abstraction from methyl groups by incident UV radiation.[20] The unstable free radicals generated in polycarbonate react with Tinuvin 770, producing stable free radicals in the probe, which are detected by ESR analysis.



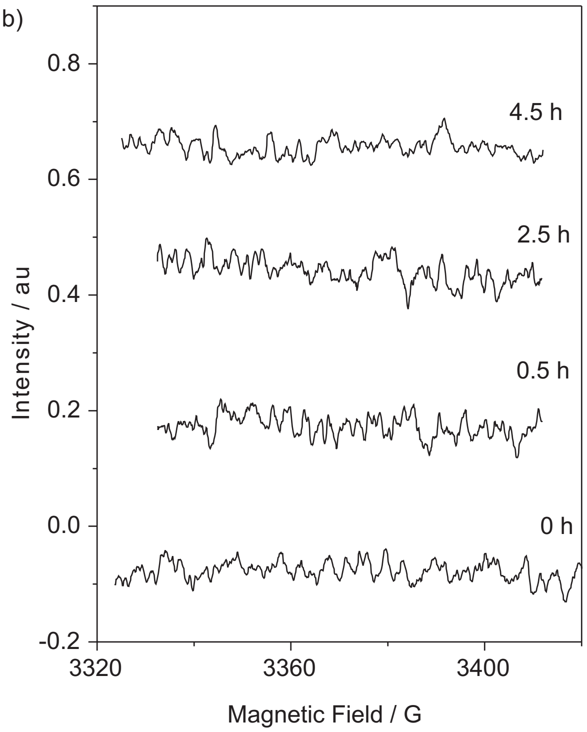


Figure 10. ESR spectra of Tinuvin 770 solutions after UV irradiation: a) in presence of bismuth vanadate, b) in presence of anthraquinone.

Figure 10 shows the sequence of ESR spectra of the Tinuvin 770 solution irradiated in the presence of $BiVO_4$ pigment and of anthraquinone dye.

The presence of $BiVO_4$ pigment in Tinuvin 770 solution produces the piperidinoxyl signal in the ESR spectra (Figure 10a) as also occurs for polycarbonate, although in the latter a more prominent signal can be recognized. The signal observed for $BiVO_4$ solution is proof of the production of free radicals in the Tinuvin 770. This process could be caused by the production of reactive chemical species in solution such as singlet oxygen ($^1O_2$) mediated by $BiVO_4$ or by a direct oxidation-reduction reaction between $BiVO_4$ and Tinuvin 770. On the other hand, when the experiment is carried out in the presence of anthraquinone dye, no modification in the ESR spectra is verified during UV irradiation (Figure 10b), showing that anthraquinone dye should not be a producer of reactive chemical species or a reactive agent itself. In order to understand the action of $BiVO_4$ under oxidation of the Tinuvin 770, a solution of Tinuvin 770 was irradiated in presence of both $BiVO_4$ and sodium azide (Figure 11). Sodium azide is known as a singlet oxygen inhibitor that may quench the piperidoxyl signal if this was produced by singlet oxygen.

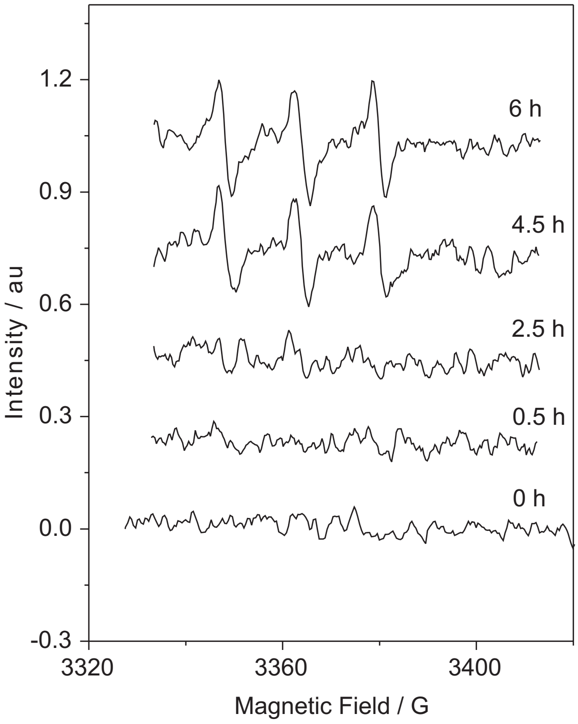


Figure 11. ESR spectra of a Tinuvin 770 solution containing bismuth vanadate pigment and sodium azide after UV irradiation.

The ESR signal was not inhibited by the presence of sodium azide. Therefore, bismuth vanadate should

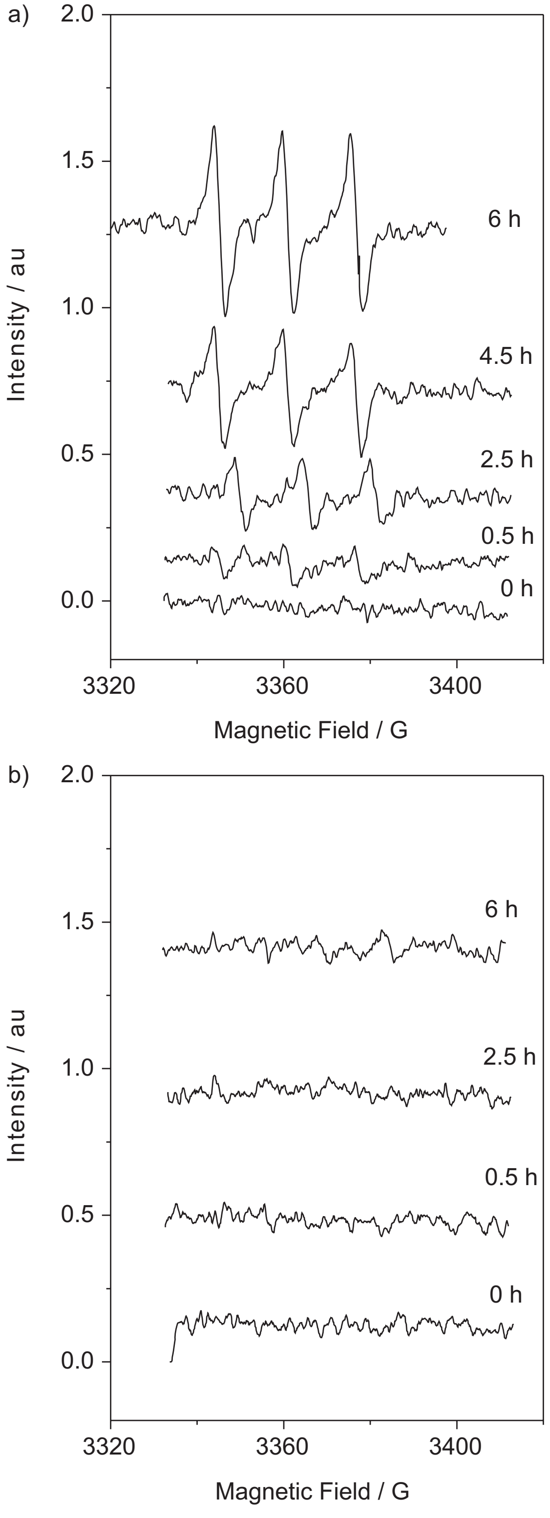


Figure 12. ESR spectra of Tinuvin 770 solutions after UV irradiation: a) containing polycarbonate and bismuth vanadate pigment, b) containing polycarbonate and anthraquinone dye.

not catalyst singlet oxygen production, and the ESR signal shown in Figure 10a is the consequence of a direct reaction between $BiVO_4$ and Tinuvin 770 under UV irradiation.

ESR spectra of Tinuvin 770 containing simultaneously polycarbonate and one of the colorants were also recorded. These spectra are shown in Figure 12.

The irradiation of Tinuvin 770 solutions in the presence of polycarbonate and $BiVO_4$ resulted in the piperidoxyl signal that can be associated to the action of either polycarbonate or $BiVO_4$ (Figure 12a). In presence of polycarbonate and anthraquinone dye no signal is obtained (Figure 12b). An intense piperidoxyl signal resulting from the action of polycarbonate on tinuvin 770 could be expected in the ESR spectra in Figure 12b, similar to Figure 9b if no action of anthraquinone had occurred. Moreover, the effect of the anthraquinone dye on the polycarbonate properties during the photodegradation process is consistent with these observations. Thus, the anthraquinone dye probably stabilizes the polycarbonate against photodegradation through deactivation mechanisms of the polycarbonate-excited states.

Conclusions

The presence of bismuth vanadate pigment makes polycarbonate more susceptible to photodegradation under accelerated aging with UVA radiation. The possible mechanism of the bismuth vanadate pigment on polycarbonate photodegradation involve a direct chemical reaction between polymer and pigment, resulting in both polymer and pigment degradation.

The presence of dye changes the mechanism of the polycarbonate photodegradation through possible desactivaction of the excited states.

Acknowledgments

The authors would like to thank GE Plastics South America and Ciba Specialty Chemicals for supplying the materials and FAPESP (Proc. No. 00/14722-8) for financial support.

References

1. Herbst, W.; Hunger, K.; *Industrial Organic Pigments: Production, Properties, Applications*, 2nd ed., Weinheim: Verlagsgesellschaft Mbh, 1997.
2. Völz, H. G.; *Industrial Color Testing: Fundamentals and Techniques*; Weinheim: Verlagsgesellschaft mbh, 1997.
3. Saron, C.; Felisberti, M. I.; *Quim. Nova* **2006**, *29*, 124.
4. Saron, C.; Zulli, F.; Giordano, M.; Felisberti, M. I.; *Polym. Degrad. Stab.* **2006**, *91*, 3301.
5. Saron, C.; Zulli, F.; Giordano, M.; Felisberti, M. I.; *Polym. Degrad. Stab.* in press.
6. Galembeck, A.; Alves, O. L.; *J. Mater. Sci.* **2002**, *37*, 1923.

7. Tang, J.; Zou, Z.; Ye, J.*; Catalysis Lett*. **2004**, *92*, 53.
8. Tokunaga, S.; Kato, H.; Kudo, A.; *Chem. Mater.* **2001**, *13*, 4624.
9. Kudo, A.; Omori, K.; Kato, H.; *J. Am. Chem. Soc.* **1999**, *121*, 11459.
10. Ye, J.; Zou, Z.; Arakawa, H.; Oshikiri, M.; Shimoda, M.; Matsushita, A.; Shishido, T.; *J. Photochem. Photobiol. A*. **2002**, *148*, 79.
11. Tsuji, I.; Kudo, A.; *J. Photochem. Photobiol. A.* **2003**, *156*, 249.
12. Oshikiri, M.; Boero, M.; Ye, J.; Zou, Z.; Kido, G.; *J. Chem. Phys.* **2002**, *117*, 7913.
13. Itoh, T.; Yamaji, M.; Shizuka, H.; *Spectrochim. Acta A* **2002**, *58*, 397.
14. Borst, H. U.; Kelemen, J.; Fabian, J.; Nepras, M.; Kramer, H. E, A.; *J. Photochem. Photobiol. A* **1992**, *69*, 97.
15. Ma, J.; Song, W.; Chen, C.; Ma, J.; Tang, Y.; *Environ. Sci. Technol.* **2005**, *39*, 5810.
16. Saquib, M.; Muneer, M.; *Dyes and Pigments* **2002**, *53*, 237.
17. Sivalingam, G.; Madras, G.; *Appl. Catalysis A.* **2004**, *269*, 81.
18. Rivaton, A.; *Angew. Macromol. Chemie* **1994**, *216*, 147.
19. Nichols, M. E.; Peters, C. A.; *Polym. Degrad. Stab.* **2002**, *75*, 439.
20. Rivaton, A.; Mailhot, B.; Soulestin, J.; Varghese, H.; Gardette, J. L.; *Polym. Degrad. Stab.* **2002**, *75*, 17.
21. Saron, C.; Felisberti, M. I.; Sanchez, E. M. S.; *Br PI 0200.366.0*, **2002**.
22. Allen, N. S.; Edge, M.; *Fundamentals of Polymer Degradation and Stabilization.* Applied Science: Manchester, 1992.
23. Thomas, J. L.; Allen, N. S.; *Dyes and Pigments* **2002**, *53*, 195.
24. Jang, B. N.; Wilkie, C. A.; *Thermochim. Acta* **2005**, *426*, 73.
25. Kuehni, R.G.; *Color: An Introduction to Practice and Principle*, John Wiley & Sons: New York, 1997.
26. Technical Report: Ciba Speciality Chemicals.Polymer Additives, *Ciba® Tinuvin® 770,* Nov. 1999.
27. Chen, Y.; Xu, S.; Li, L.; Zhang, M.; Shen, J.; Shen, T.; *Dyes and Pigments* **2001**, *51*, 63.
28. Rajendran, M.; Ramasamy, S.; Rajamanickam, C.; Gandhidasan, R.; Murugesan, R.; *Biochim. Biophys. Acta Gen. Subj*. **2003**, *1622*, 65.

Received: December 14, 2006
Web Release Date: July 24, 2007

FAPESP helped in meeting the publication costs of this article.