Synthesis and Characterization of Hindered Amine Light Stabilizers Based on End Functionalization of Polypropylene

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ABSTRACT: A polymeric hindered amine light stabilizer (HALS), where HALS moiety was attached at the terminal end of the polypropylene chain via end-functionalized vinylidine PP through simple organic reactions, was synthesized. It comprises the synthesis of vinylidine-terminated polypropylene by using Cp_2ZrCl_2/MAO as catalyst system and epoxidation of vinylidene polypropylene. The final product was synthesized by carrying out the reaction between epoxy end functionalized polypropylene and 4-amino-2,2,6,6-tetrametyl piperidine. The final product was characterized by using ^{1}H NMR, ^{13}C NMR, and FT-IR spectra. Functionality was calculated by using vapor phase osmometry and ^{1}H NMR. The solubility and diffusion coefficient of the product were calculated and also its stabilization performance was checked. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1596–1602, 2007

Key words: end functionalization; functionalization of polymers; polypropylene; polymeric HALS; vinylidine and photostabilization

INTRODUCTION

The degradation of polymers begins as soon as it is synthesized and is increased by residual stresses left during molding processes. This degradation can be accelerated by exposure to light (especially UV), humidity, oxygen, heat, bacteria, and stress. It is well known that hindered amine light stabilizers (HALS) based on piperidine are efficient to protect polymers from light.[1,2] The efficiency of the stabilizer depends on their solubility, compatibility, and dispersability in the polymer matrix. Low molecular weight HALS are volatile and get decomposed during processing to emit harmful amines and also can easily migrate to the solvents during usage leading to decrease in photostabilization efficiency. These drawbacks caused by the low molecular HALS can be overcome through the use of polymeric HALS. The polymeric stabilizers, made by copolymerization of a monomer bearing HALS group with styrene and/or acrylate having high polarity, are less effective in hydrophobic polymers like polyethylene and polypropylene probably because of the poor dispersion. So, there is a demand for polymeric stabilizers containing HALS moieties, which can be fairly dispersed in the polymer and do not easily migrate to solvents. Wilen et al.[3] reported the copolymerization of 4-(hex-5-enyl)-2,2,6,6-tetramethyl piperidine with polypropylene by using a heterogeneous catalyst. Several long chain HALS monomers with poly(propylene)[4] and also a long chain HALS monomer were copolymerized with ethylene by using metallocene/MAO catalyst system.[5] Previously, we prepared a HALS end functionalized poly-(ethylene-*alt*-propylene) copolymer by terminating the living anionic polymerization of isoprene with 4(2,3-epoxy propoxy)-1,2,2,6,6-pentamethyl piperidine followed by hydrogenation.[6] The efficient stabilizer should exhibit better miscibility, compatibility, and less migration from polymer matrix to the solvent. It will be worthwhile to synthesize a polymeric stabilizer with appreciable molecular weight and better compatibility so that it can disperse well through out the matrix to show better performance.

In this article, for the first time, a novel end functionalized polymeric HALS has been synthesized based on end functionalization of vinylidene polypropylene oligomers via simple organic reactions. It involves synthesis of vinylidene chain end polypropylene oligomers by using Cp_2ZrCl_2/MAO (biscyclopentadienylzirconium dichloride/methylaluminoxane) as catalyst system and epoxidation of vinylidene polypropylene. In the final step, the epoxy end functionalized polypropylene was reacted with 4-amino-2,2,6,6-tetrametyl piperidine to yield final product. It was revealed that this stabilizer may give both compatibility and dispersibility as well as good light stability in the polyolefins.

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Materials

Cp_2ZrCl_2 and MAO were obtained from Witco, Bergkamen, Germany and used as received. Toluene, 4-amino-2,2,6,6-tetramethyl piperidine, and chlorobenzene are used as obtained from Merck chemicals. Toluene was dried over sodium wire prior to use.

Preparation of vinylidine terminated polypropylene

Polymerizations were carried out in a 100 mL glass reactor (Buchi, Uster, Switzerland), equipped with a magnetic bar and temperature control. The reactor was purged with nitrogen and followed by propylene. To this reactor, moisture-free toluene and methylalumoxane (10 wt % in toluene) were added. The mixture was stirred for 15 min, the pressure of the reactor was increased to corresponding pressure during the polymerization with propylene, and the solution was allowed to saturate with propylene while the reactor was kept at a constant temperature (30°C). The polymerization was initiated by the addition of 3.4 $\times 10^{-3}M$ solution (2.8 $\times 10^{-6}$ mol, stock solution prepared by dissolving 10 mg in 10 mL of toluene) of biscyclopentadienyl zirconium dichloride into the reactor. During the polymerization, propylene was continuously fed into the reactor to maintain the total pressure at a constant pressure. The reaction was terminated after 2 h with solution of hydrochloric acid in methanol. After termination of the reaction, the oligomer solution was separated from methanol. The viscous oligomer solution was transferred to the separating funnel and washed several times with methanol and the solvent was removed under vacuum.

Synthesis of polypropylene end-functionalized with HALS

The synthesis of polypropylene end-functionalized with HALS was carried out by epoxidation of vinylidene terminated polypropylene and followed by reacting it with 4-amino-2,2,6,6-tetramethyl piperidine (Scheme 1).

A two necked 250 mL round bottom flask containing a magnetic stirring bar fitted with a septum adapter and nitrogen inlet was taken. To this, 50 mL of dry DCM was added and followed by 5 g of polypropylene oligomer. To this mixture, 2.5 equivalents of m-chloroperbenzoic acid was introduced and the reaction mixture stirred for 12 h. The above reaction mixture was quenched by the addition of $NaHCO_3$ saturated aqueous solution to remove excess m-chloroperbenzoic acid, and the solution was washed several times with $NaHCO_3$ aqueous solution. Then the polymer was recovered by evaporation of DCM.
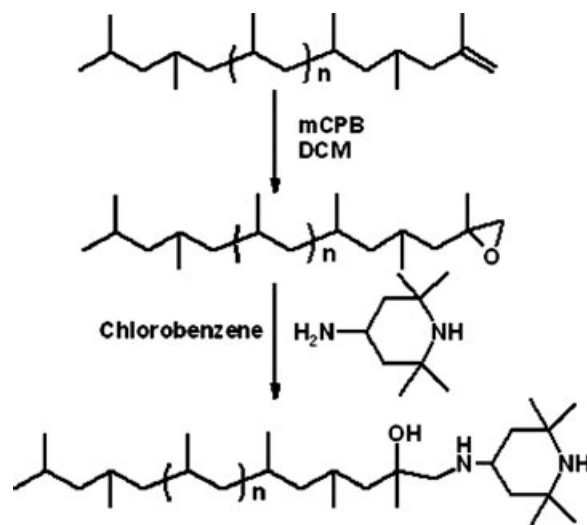
Scheme 1 Synthesis of HALS end functionalized polypropylene.

A 250 mL two necked round bottom flask containing magnetic stirring bar was fitted with condenser and a nitrogen inlet. To this, 40 mL of dry chlorobenzene was added and followed by the addition of 4 g of epoxy functionalized polypropylene. Subsequently, 2.5 equivalents of 4-amino-2,2,6,6-tetramethyl piperidine was added and the reaction temperature maintained at 80°C and continued for 36 h. The above reaction was quenched by the addition of water and washed several times with water. The desired product was obtained by evaporating the solvent.

Mixing of stabilizers

Separately a low molecular weight HALS (Tinuvin 770), polymeric HALS are mixed with additive-free polypropylene. The mixing was carried out with different concentrations of stabilizer and powder polymer in micro-compounder (DSM, Netherlands) in 4 g scale at 170°C for 5 min. The films of the stabilized polypropylene were prepared by pressing at 170°C in compression mold. The thickness of films was found 80 μm. All the samples were irradiated in an irradiation chamber, SEPAP 12/24, as described elsewhere.[7]

Diffusion experiments

Diffusion measurements were carried out by using the system described by Roe et. al.[8] A stack of 25 unstabilized (thickness about 60 μm) films of i-PP were prepared by heating stack in a hydraulic press at 75°C for 3 min. The obtained stack was compact, transparent, and without any air bubbles. The additive sources were prepared by mixing the stabilizers (Tinuvin 770 and polymeric HALS) by melt blending in twin screw micro-compounder and about 0.2 mm

thickness of sheet was made by melt pressing. For diffusion studies, the unstabilized film stack was placed with additive source and then pressed between two steel plates by using a clamp. Then, the whole set up was put into an oven, which is flushed with nitrogen under isothermal conditions at definite temperature and for given time. Stabilizer concentrations in the films were determined by using UV spectroscopy and calibration was made in n-heptane solution. The film next to the additive source was excluded in the calculation to avoid errors caused by additive adsorption.

The diffusion coefficient was determined using the method given by Moisan.[9] This method treats the process as a one-dimensional diffusion problem. It is assumed that at the start of the experiment ($t = 0$) the additive concentration is $c = 0$ at any distance from the additive source ($x > 0$) and that during the experiment ($t > 0$) concentration of the additive in the additive source ($x < 0$) remains constant and equals the solubility ($c = S$). Concentration at position x and time t is described by eq. (1).

$$c(x, t) = S[1 - \mathrm{erf}(x/K)] \quad (1)$$

where K is determined by the time, and the diffusion coefficient D and can be given by eq. (2),

$$K = 2\sqrt{Dt} \quad (2)$$

For calculation of the parameters D and S from the concentration profile an interactive least-square curve-fitting program was used. The solubility is given directly by this calculation.

Characterization

The number average molecular weight (M_n) of HALS functionalized polypropylene was calculated by using vapor phase osmometry (VPO) as well as ^{1}H NMR spectra. The number average molecular weight was calculated by ^{1}H NMR based on the protons of vinylidine methylene group. Structural analysis was carried out by using ^{1}H NMR, ^{13}C NMR, and FT-IR spectra. The number average degree of functionality was calculated as $F_n = M_n$ by VPO/M_n by ^{1}H NMR. FT-IR spectra were obtained from Perkin-Elmer 16 PC spectrophotometer in chloroform solution. Quantitative ^{1}H and ^{13}C NMR were recorded at 30°C in CDCl$_3$ on a Bruker MSL 500 model spectrometer operating at 75.5 MHz. The number average molecular weight (M_n) was determined by Knauer-7000 VPO at 30°C in chloroform using benzil as standard.

RESULTS AND DISCUSSION

Vinylidine terminated poly(propylene)s were synthesized using Cp$_2$ZrCl$_2$/MAO as catalyst system as

TABLE I
Synthesis of Polypropylene Oligomers

Run no.	Al/Zr	Polypropylene M_n		Epoxy functionalized polypropylene (EPP)[a] M_n		End groups F_n (mol %)	EPP (mol × 10^3)	HALS functionalized polypropylene[b] Yield (g)	M_n		F_n (mol %), a/b
		VPO	NMR	VPO	NMR				VPO, a	NMR, b	
1	5000	995	1000	1010	1056	95.6	5	4.8	1221	1320	92.5
2	2000	2476	2500	2490	2665	93.4	2	4.6	2653	2925	90.8
3	1000	3480	3550	3502	3800	92.0	1	4.5	3745	4210	89.0

Catalyst: Cp$_2$ZrCl$_2$, 2.8 × 10^{-6} mol; pressure: 3 At; time: 2 h, temperature: 30°C.
[a] 2.5 equalents of mCPB.
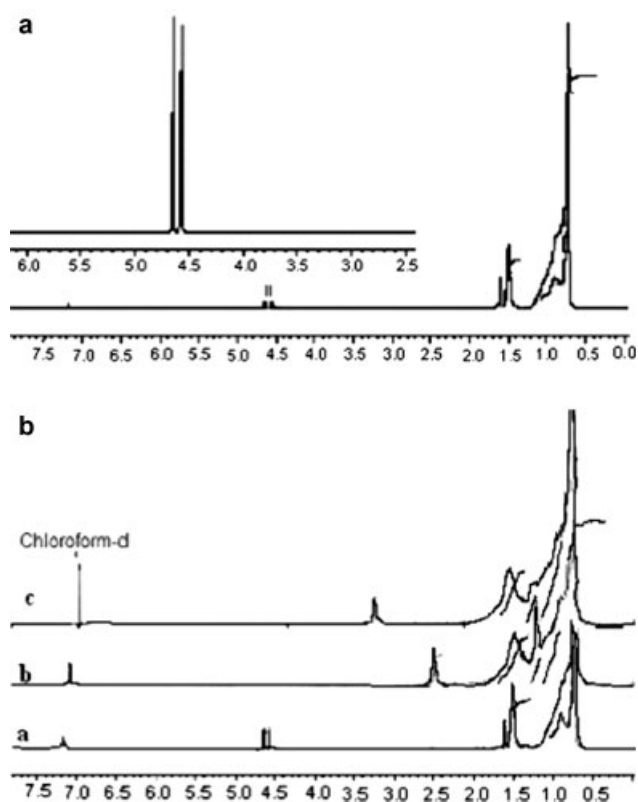[b] 2.2 equavelents of 4-amino-2,2,6,6-tetramethyl piperidine.

Figure 1 (A) ^{1}H NMR (500 MHz) of vinylidine terminated polypropylene (from run no. 1, Table I). (B) ^{1}H NMR (500 MHz) spectra of (a) vinylidine terminated polypropylene, (b) epoxy end functionalized polypropylene, and (c) HALS end functionalized polypropylene (run no. 1).

described in the experimental part. The polymerizations were carried out at different Al/Zr ratios to yield different molecular weights of polypropylene. The obtained polypropylene oligomers are viscous liquids. The polymerization and characterization data are presented in Table I. ^{1}H NMR spectrum [Fig. 1(A)] of the oligomer samples thus obtained showed two peaks at 4.57 and 4.64 ppm corresponding to the vinylidine unsaturation.[10,11] There are no peaks

around 5.2 ppm, which could have been due to vinyl unsaturation. The absence of a peak around 5.2 ppm even after 1000 scans and the presence of peaks only at 4.57 and 4.64 ppm shows that the samples prepared have predominantly vinylidine unsaturation. The molecular weights calculated by ^{1}H NMR spectra and molecular weights calculated by VPO are comparable and implies that each chain end has the vinylidine functionality.

The synthesis of epoxy-functionalized polypropylene was performed by the reaction between polypropylene with vinylidine group and *m*-cloroperbenzoic acid, and the epoxy groups were introduced at the chain end. As shown in Figure 1(B), the ^{1}H NMR spectra of epoxy functionalized PP showed a peak at $\delta = 2.60$ ppm, which confirms the presence of epoxy group. The disappearance of peaks at 4.57 and 4.64 ppm shows that all the vinylidine groups were reacted to give epoxy group. The functionality of the epoxy groups was calculated and tabulated in Table I. In the final step, the synthesis of HALS functionalized polypropylene was performed between epoxy end functionalized polypropylene and 4-amino-2,2,6,6-tetramethyl piperidine. It has been reported that epoxides readily react with amines in stoichiometric conditions.[12] The number average molecular weight (M_n) of the final product was calculated by using ^{1}H NMR based on the methylene protons adjacent to amine group, which was found at $\delta = 3.25$ ppm. The functionality was calculated as mentioned above and was found to be 89–93% (Table I). From Table I, it is also found that the functionality was decreased with increase in the molecular weight. The final product was also characterized by using ^{13}C NMR and FT-IR. The ^{13}C NMR spectrum of the HALS end functionalized polypropylene is shown in Figure 2. The compound is also characterized for FTIR. From Figure 3, it is clearly seen that the peaks at 3463 cm^{-1} (N—H and —OH) and 1240 cm^{-1} (C—N) have appeared and the peak at 1085 cm^{-1} corresponding to epoxide has disappeared. In the first step, formation of epoxide was
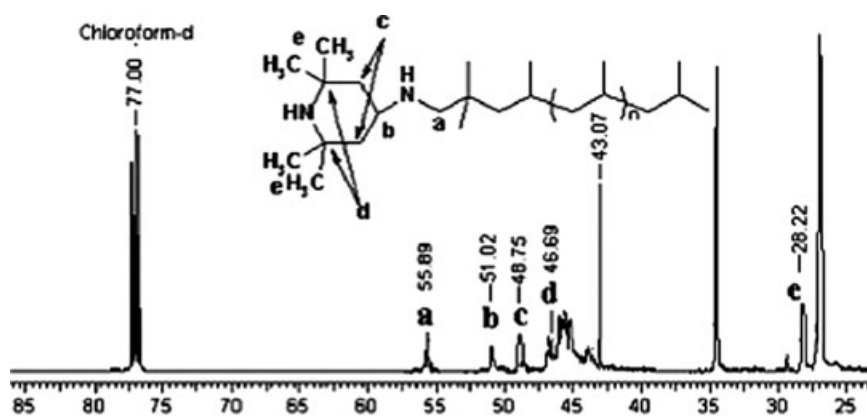

Figure 2 ^{13}C NMR of HALS functionalized polypropylene (run no. 1).
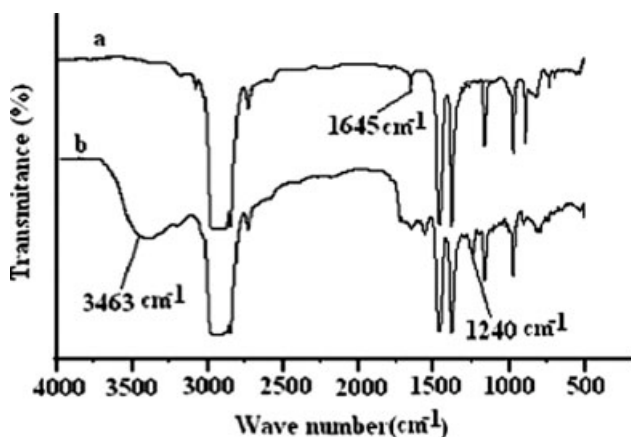
Figure 3 FTIR spectra of (a) vinylidine terminated polypropylene, (b) epoxy terminated polypropylene, and (c) HALS end functionalized polypropylene (run no. 1).

confirmed by disappearance of bands at 1645 (C=C) and 892 cm^{-1} (C—H vinylidine bend) of vinylidine PP and appearance of new band at 1085 cm^{-1} epoxide (C—O—C). This FTIR result supports the formation of the final product.

Diffusion of HALS

Figure 4 shows the concentration profiles of Tinuvin 770 and P-HALS in a film stack of i-PP after 48 h at 60°C and 100 h at 80°C, respectively. As can be seen, there is a very good fit between the experimental data and the theoretical curve obtained from Eq. (1). Solubilities (S) of the additives in i-PP sample was determined from a concentration profile plot by using the equation $C(X,t) = S[1 - \mathrm{eft}(X/K)]$ and a least-square curve fitting program. Extrapolation of this curve to zero distance ($X = 0$) gives S. Diffusion coefficient (D) calculated from the plots is shown in Table II. The
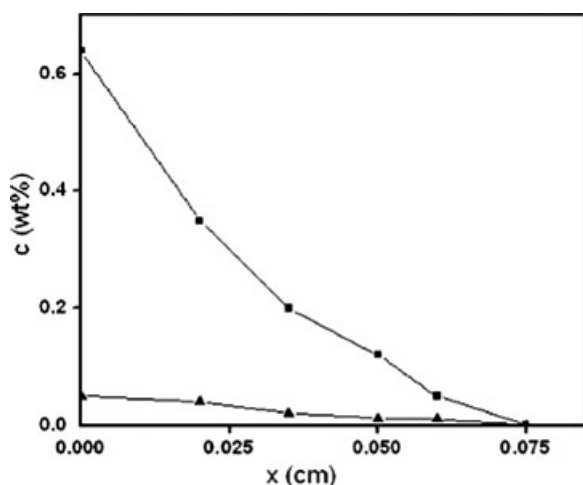
TABLE II
Diffusion Coefficient (D) and Solubility of Tinuvin 770 and Polymeric HALS in i-PP

Polymer	Tinuvin 770		Polymeric HALS	
	$D \times 10^{10}$ (cm^2/s)	Solubility (S) (wt %)	$D \times 10^{10}$ (cm^2/s)	Solubility (S) (wt %)
i-PP	25	0.9	5.4	0.03

results show that polymeric HALS has a diffusion coefficient of 5.3×10^{-10} cm^{2}s^{-1} and 0.03 wt % solubility, which is about five times lower than Tinuvin 770. This is due to the higher molecular weight of the former, which restricts additive diffusion and solubility.

Malik et al.[13] reported that Chimassorb 944 (oligomeric HALS) showed no measurable diffusion up to 10 months (7300 h) at room temperature. The piperidine skeleton in Chimassorb 944 is bound in position 4 through a nitrogen atom. They suggested that the attachment of piperidine through nitrogen gives immeasurable penetration of this additive into the polymer stack. It was also suggested that the diffusion coefficient (D) and solubility (S) of an additive are reduced with an increase of molecular weight and depends on the difference between the polarity of the polymer molecule and that of the additive.

Photostabilizing efficiency of polymeric HALS

The synthesized polymeric HALS was tested as light stabilizer in i-PP and compared with commercial HALS (Tinuvin 770) and Chimassorb 944 by measuring the carbonyl absorbance at 1720 cm^{-1}. As shown in Figure 5, plots of carbonyl absorbance vs. irradiation time in i-PP samples stabilized with Tinuvin 770 at three different concentrations. At lower con-
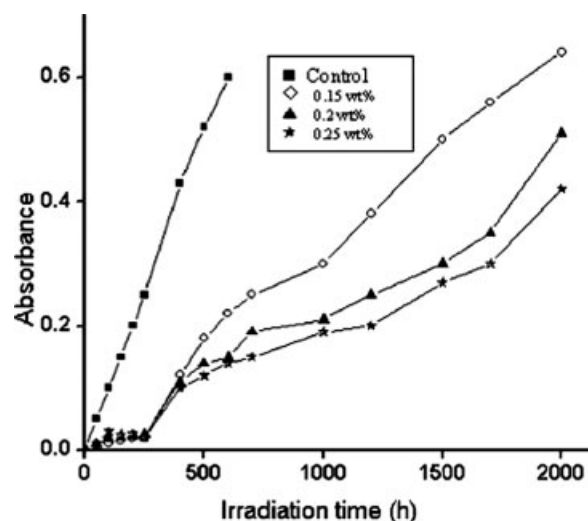

Figure 4 Concentration distribution of Tinuvin 770 in iPP and polymeric HLAS in iPP.

Figure 5 Carbonyl index versus irradiation time (h) in iPP films at different concentrations stabilized with Tinuvin 770.
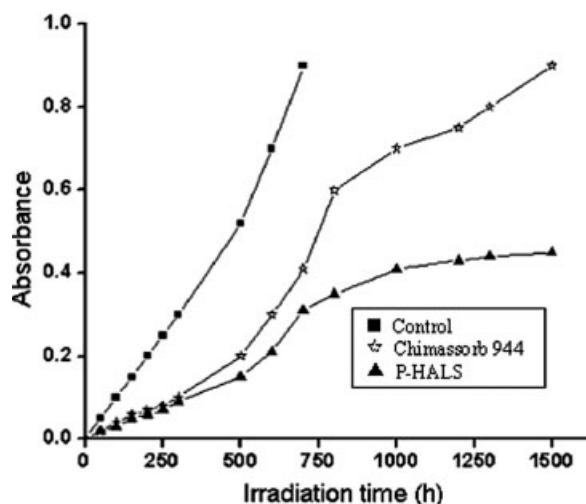
Figure 6 Carbonyl index versus irradiation time (h) in iPP films containing Chimassorb 944 and polymeric HALS at 0.15 wt %.

centration level, the carbonyl group formation is more in the case of samples stabilized with Tinuvin 770 when compared with polymeric HALS for longer times. In Figure 6, the rate of carbonyl absorbance was plotted against irradiation time at HALS stabilizer (polymeric HALS and Chimassorb 944) unit concentration of 0.15 wt %. The unprotected i-PP film showed a rapid increase in the carbonyl absorbance after only 25 h irradiation without any induction period, whereas in the case of stabilized polymer films containing 0.15 wt % of stabilizer, the carbonyl absorbance was observed only after induction period of 300 h. The increase in carbonyl absorbance is almost linear in polymeric HALS stabilized films, whereas in case of Tinuvin 770 and other Chimassorb 944 stabilized films
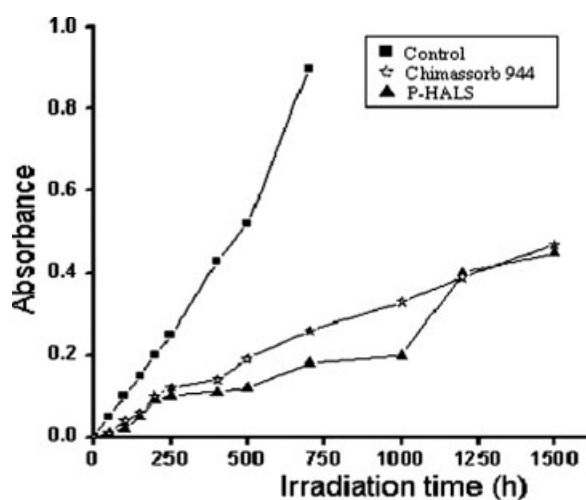
the increase in carbonyl absorbance is exponential (Figs. 4 and 5), and reaches an asymptotic value around 1000 h irradiation. This can be understood based on the fact that low molecular weight Tinuvin 770 undergoes migration and surface evaporation at longer irradiation time whereas Chimassorb 944 showed negligible diffusion and less solubility in polyolefins because of high molecular weight and the polar nature of the backbone polymer. On the other hand, polymeric HALS has significant diffusion compared with Chimassorb 944 stabilizer and thus, it remains in the polymer for long time to be able to exert its stabilizer behavior.

Figure 7 shows the carbonyl absorbance with irradiation time in i-PP films at higher stabilizer concentration of 0.2 wt %. The carbonyl group formation was observed after an induction period of 400 h in all the stabilized polymer films. The carbonyl absorbance is almost similar in the case of both polymeric HALS and Chimassorb 944. At even higher concentration levels (stabilizer unit concentration 0.3 wt %), the carbonyl group formation was observed after 500 h. However, there is no significant difference in the photostabilizing efficiency of either polymeric HALS or Chimassorb 944 (Fig. 8).

The difference in effectiveness between polymeric HALS and Chimassorb 944, as a function of stabilizer concentration, is an indication and an important role played by the ability of polymeric stabilizer to diffuse into the matrix. At a stabilizer concentration of 0.2 wt % of polymer, polymeric HALS shows a superior stabilizer performance compared with Chimassorb 944. Polymeric HALS, containing propylene units in the backbone has a higher degree of compatibility with i-PP resulting in higher solubility and greater diffusivity. This enables the polymeric HALS to distribute
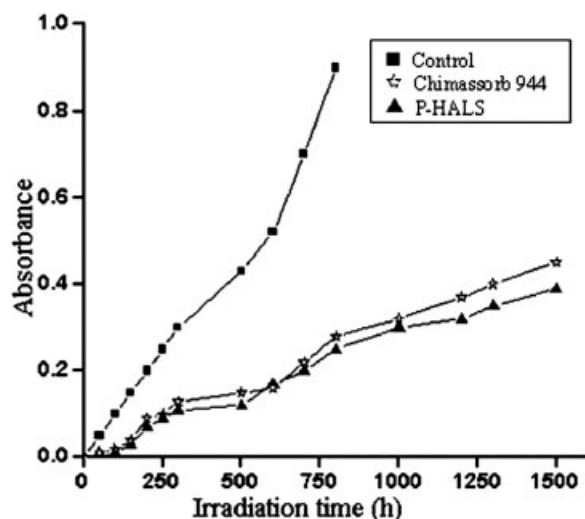

Figure 7 Carbonyl index versus irradiation time (h) in iPP films containing Chimassorb 944 and polymeric HALS at 0.20 wt %.

Figure 8 Carbonyl index versus irradiation time (h) in iPP films containing Chimassorb 944 and polymeric HALS at 0.25 wt %.

itself evenly throughout the matrix. On the contrary, Chimassorb 944 has a poor compatibility with the matrix limiting its diffusivity. This leads to a concentration gradient of the stabilizer in the bulk of the polymer matrix. As a result, the performance of Chimassorb 944, it is inferior to polymeric HALS.

At high levels of HALS concentration, the stabilizer will distribute itself throughout the polymer matrix, and factors such as molecular weight, polarity, and diffusion are likely to play a lesser role. Therefore, polymeric HALS, Tinuvin 770, and Chimassorb 944 show similar effects on photostabilization on i-PP.

CONCLUSIONS

The end functionalization of polyolefins was utilized for the first time for synthesizing a novel end functionalized polymeric stabilizer of vinylidene poly(propylene). The vinylidine-terminated polypropylenes were synthesized by Cp_2ZrCl_2/MAO catalyst system and analyzed by ^{1}H NMR. The HALS end functionalized poly(propylene) was successfully synthesized with higher functionality. These HALS end functionalized polypropylene stabilizer showed a marginal improved stability when compared with commercial high molecular weight stabilizer Chimassorb 944. The polymeric HALS showed a better performance compared with Tinuvin 770 at practically used concentrations (0.2 wt %) even at longer irradiation time.

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