

Synthesis of New Polymeric Hindered Amine Light Stabilizers: Performance Evaluation in Styrenic Polymers

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ABSTRACT: Polymeric hindered amine light stabilizers (HALSs), in which the HALS functionality was attached to the terminal isocyanate chain end of poly(styryl-*co*-styryl isocyanate), were synthesized by a two-step process. First, cinnamoyl azide was prepared and copolymerized with styrene by a free-radical copolymerization method. Polymeric low-molecular-weight and high-molecular-weight 2,2,6,6-tetramethyl-4-piperidinol-*graft*-poly(styryl-*co*-styryl isocyanate) and 4-amino-2,2,6,6-tetramethyl piperidine-*graft*-poly(styryl-*co*-styryl isocyanate) were synthesized by a grafting method. The photodegradation and stabilization of different grades of high-impact polystyrene (HIPS) were studied at

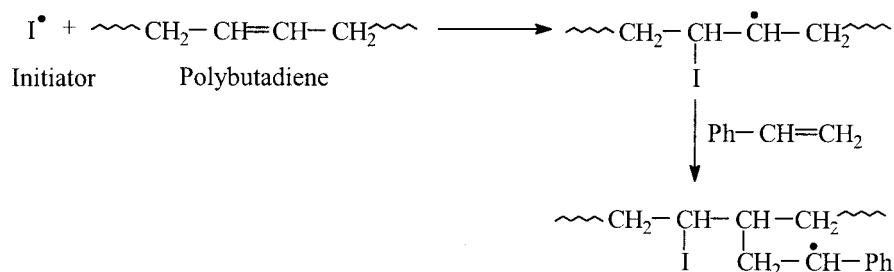
55°C in air at different time intervals, and the photostabilizing efficiency of polymeric HALSs was compared with conventional light stabilizers, such as 2,2,6,6-tetramethyl-4-piperidinol and bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate. Polymeric HALSs showed significant improvements in the photostabilization of HIPS. The solubility and diffusion coefficient of polymeric HALSs were studied. The morphological changes in HIPS caused by photooxidation were also studied. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1126–1138, 2003

Key words: additives; degradation; polystyrene; radiation

INTRODUCTION

High-impact polystyrene (HIPS) consists of a continuous glassy polystyrene (PS) matrix and an elastomeric dispersed polybutadiene (PB) phase. The dispersed PB phase is compatibilized with the glassy PS

phase by the presence of PS grafts during the synthesis. The active groups for grafting in PB are the double bonds and the methylene hydrogen at the α position. These sites are attacked by the initiator radical or by the growing PS radical.^{1,2}



The PB portion³ in HIPS is generally 3–12 wt %. Although there is a significant increase in the elongation at break and fracture resistance in PS with the addition of PB, a simultaneous reduction in the transparency and modulus is also observed.

Polymers are susceptible to degradation by oxygen when subject to a combination of UV light and heat.⁴ Scott et al.⁵ showed that rubber-modified plastics undergo a loss of physical properties when exposed to

outdoor weathering because of photooxidation. Photooxidation is also accompanied by a loss in the molecular weight and yellowing.⁶ The oxidative degradation can partially be prevented by the introduction of suitable stabilizers into the polymer matrix. During the past decade, the chemistry and synthesis of stabilizers and their mechanism of action have been studied extensively.⁷ Hindered amine light stabilizers (HALSs) have gained prominence as effective light stabilizers for a variety of polymers. The conventional stabilizers are low-molecular-weight compounds; therefore, they migrate and leach out from the polymer matrix by evaporation or extraction during processing and end use. For a polymer to have longer stability, the stabilizer must remain in its matrix in the active form; therefore, the chemical nature of the ad-

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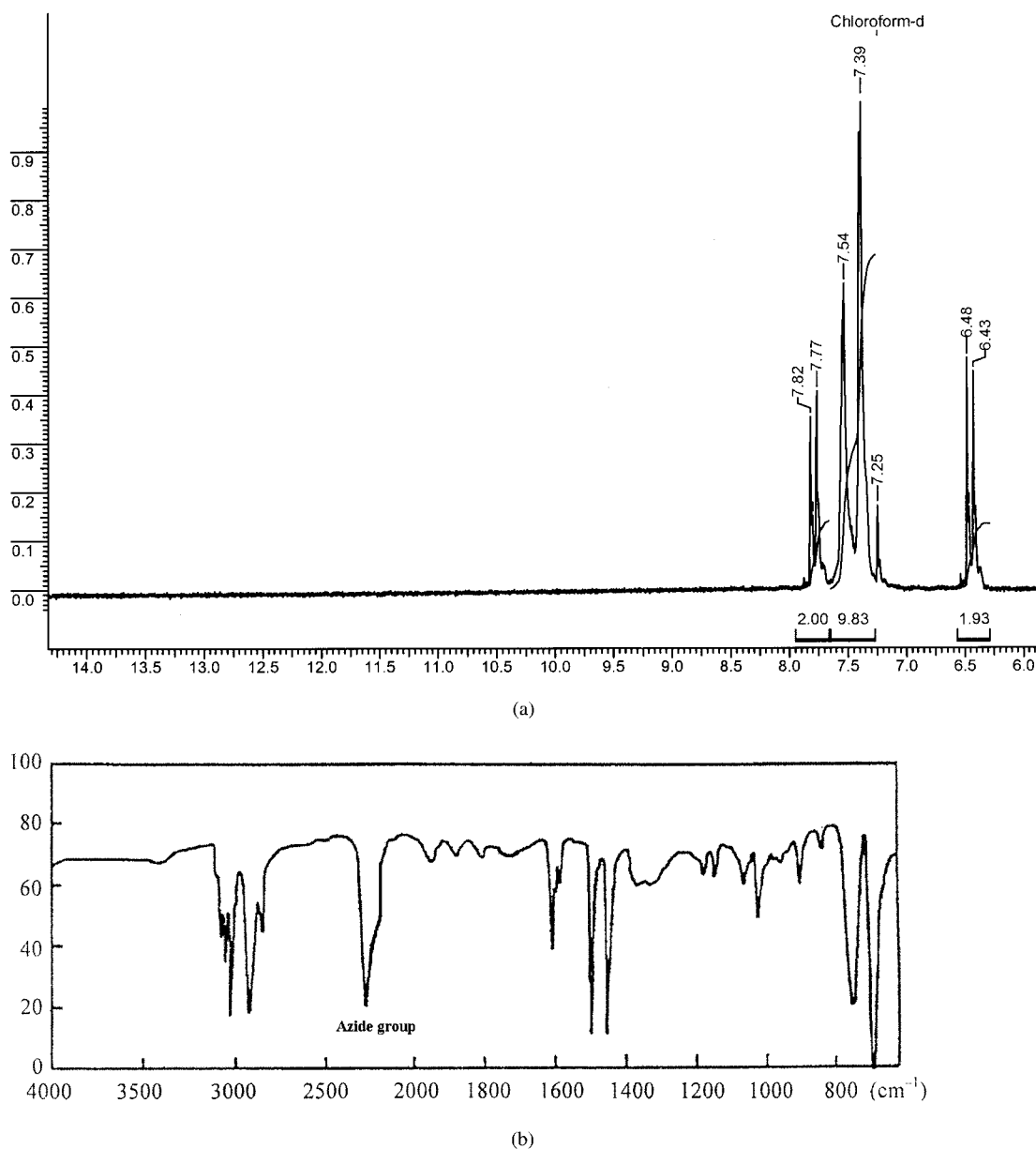


Figure 1 (a) $^1\text{H-NMR}$ and (b) FTIR spectra of cinnamoyl azide.

ditive is important. The rate of additive loss also depends on its compatibility and is controlled by its volatility, extractability, solubility, and diffusion coefficient.⁸⁻¹¹ For these properties to be improved, an additive should have a higher molecular weight, or it should be bonded to the polymeric substrate. To overcome these problems, polymeric additives are being used to enhance compatibility and stability under light and heat. HALSs are among the most effective stabilizers and are attracting worldwide scientific and industrial interest; therefore, there has been a trend toward the use of polymeric HALSs.^{12,13}

In this study, we synthesized new polymeric HALSs and evaluated their performance in HIPS. We also examined the diffusion and solubility of polymeric HALSs in HIPS matrices.

EXPERIMENTAL

Materials

We investigated two types of HIPS: HIPS-I was supplied by Polychem (India), and HIPS-8350 (HIPS-II) was obtained courtesy of Elf-Atochem (France). 2,2'-Azobisisobutyronitrile (AIBN), toluene, tetrahydrofuran (THF), and methyl ethyl ketone were purified by conventional procedures. All other reagents were analytical-grade, were obtained from Fluka AG or Aldrich (Milwaukee, WI), and were used as received. 2,2,6,6-Tetramethyl-4-piperidinol (TMC) and 4-amino-2,2,6,6-tetramethyl piperidine were obtained from Aldrich and used as received. The conventional stabilizer bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate (Tinuvin 770) was obtained from Ciba-Geigy (Mumbai, India).

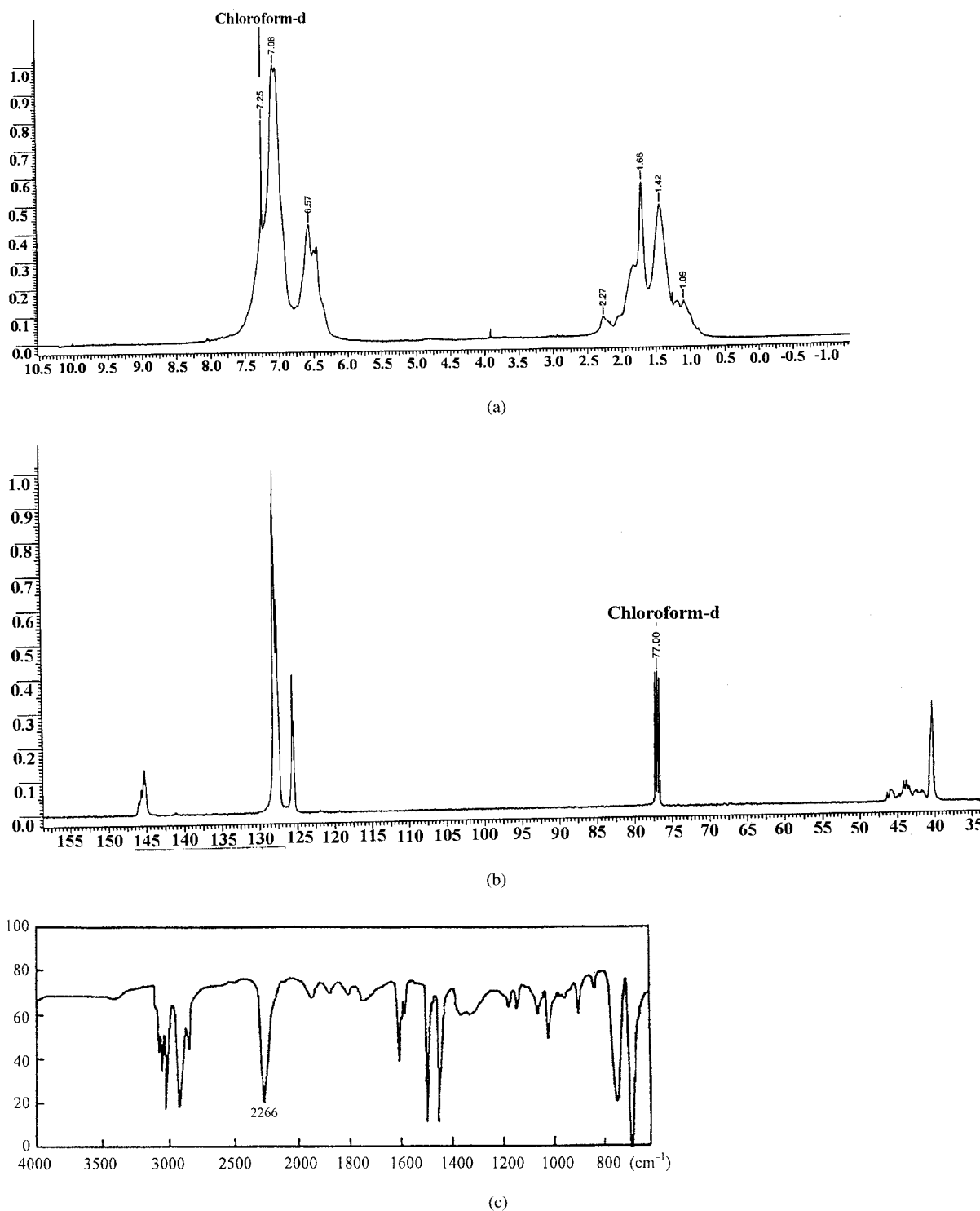


Figure 2 (a) $^1\text{H-NMR}$, (b) $^{13}\text{C-NMR}$, and (c) FTIR spectra of PSSI.

Photoirradiation

The films ($\sim 100 \mu\text{m}$) were made in a hydraulic press with a quench-cooling method at 200°C . All films were photoirradiated in SEPAP 12/24 (Materiel Physico Chimique, Neuilly/Marne, France) at 55°C . The instrument has been described elsewhere.¹⁴

Characterization

Cinnamoyl azide, a styrene-styryl isocyanate copolymer [poly(styryl-*co*-styryl isocyanate) (PSSI)], 2,2,6,6-tetramethyl-4-piperidinol-*g*-PSSI, and 4-amino-2,2,6,6-tetramethyl piperidine-*g*-PSSI were characterized by Fourier transform infrared (FTIR) spectroscopy (16

TABLE I
Parameters for Free-Radical Copolymerization of Styrene-co-Styryl Isocyanate

Polymer	Molar fraction of styrene	Time (h)	Conversion (%)	$M_n \times 10^3$	$M_w \times 10^3$	MWD
PSSI-1	0.95	24	45	3.32	10.13	3.05
PSSI-2	0.85	18	38	2.36	7.53	3.19
PSSI-3	0.90	30	43	3.77	13.07	3.47
PSSI-4	0.60	15	32	1.91	8.71	4.58

PC, PerkinElmer, Huenenberg, Switzerland); $^1\text{H}/^{13}\text{C}$ -NMR spectra were recorded with a Bruker (Germany) MSL-300 spectrometer with tetramethylsilane as the internal standard. The number-average molecular weights (M_n 's), weight-average molecular weight (M_w 's), and molecular weight distributions (MWDs) of the copolymers were determined with Waters (India) GPC-150 and GPC-II instruments with a refractive-index detector. The measurements were carried out with μ -Styragel columns (10³-, 500-, and 100-Å pore sizes) and PI gel columns (10⁴-, 10³-, 500-, and 100-Å pore sizes) at room temperature with THF as an effluent at a flow rate of 1.0 mL/min. The gel permeation

chromatography curves were analyzed with a calibration curve obtained from PS standards.

Synthesis of polymeric HALSs

Synthesis of PSSI

The copolymer synthesis involved a two-step process. *Step I: Synthesis of cinnamoyl azide*¹⁵ To a well agitated suspension of cinnamic acid (18 g, 0.1216 mol) in 120 mL of a THF/water (1:1) mixture, triethylamine (15 g, 0.1648 mol) in 30 mL of THF was added dropwise over 30 min, and the mixture was stirred for 1.5 h. The reaction tem-

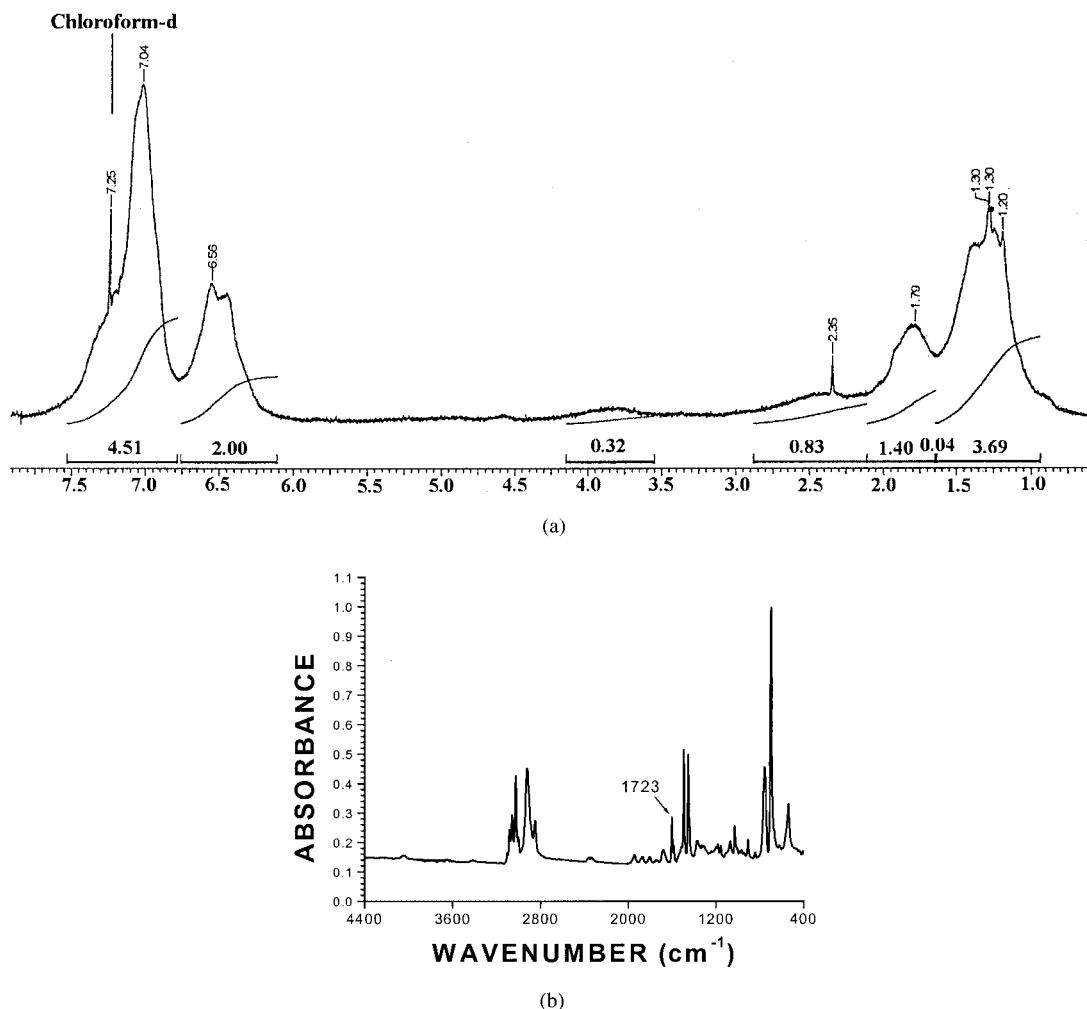
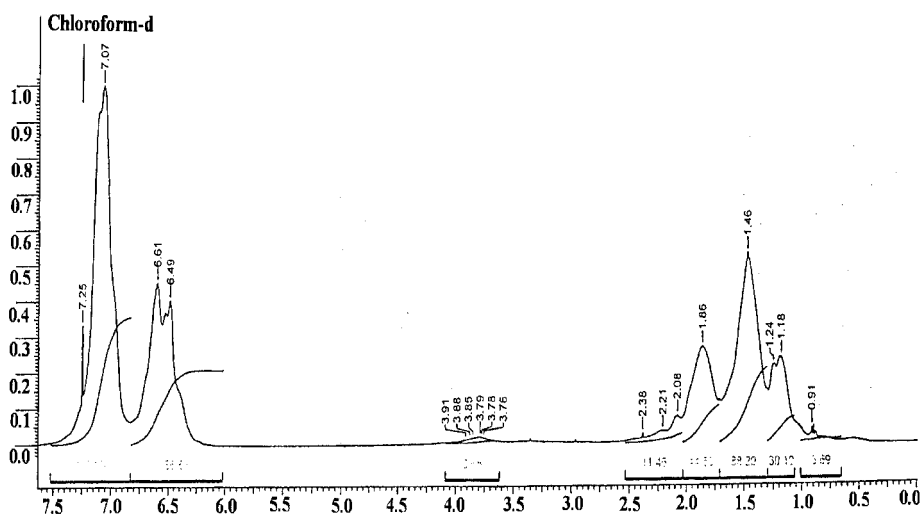
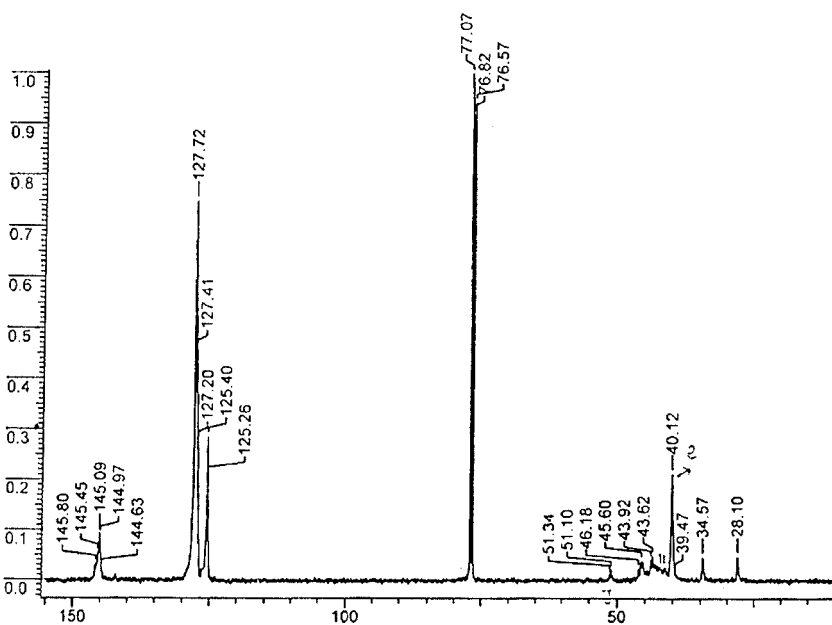


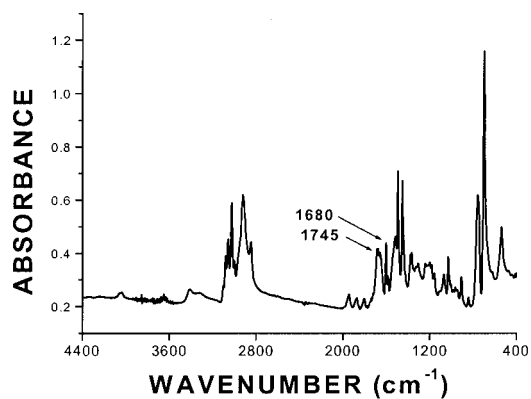
Figure 3 (a) ^1H -NMR and (b) FTIR spectra of polymeric 2,2,6,6-tetramethyl-4-piperidinol-g-PSSI (HALS-1).



(a)



(b)



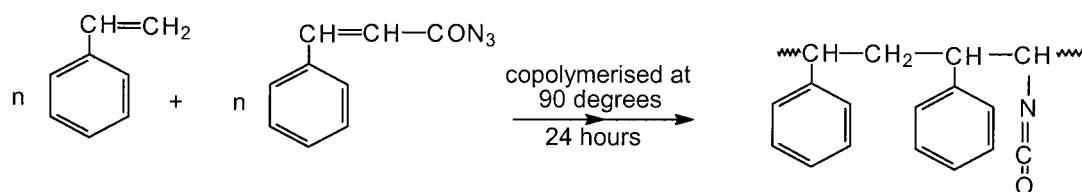
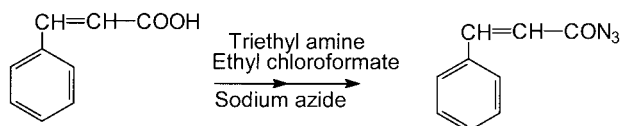
(c)

Figure 4 (a) ¹H-NMR, (b) ¹³C-NMR, and (c) FTIR spectra of polymeric 4-amino-2,2,6,6-tetramethyl piperidine-g-PSSI (HALS-3).

TABLE II
HALS Content in PSSI

Polymeric HALS	HALS (wt %)	Time of grafting (h)
HALS-1 (2,2,6,6-tetramethyl-4-piperidinol-g-PSSI)	2.26	5
HALS-2 (2,2,6,6-tetramethyl-4-piperidinol-g-PSSI)	0.50	3
HALS-3 (4-amino-2,2,6,6-tetramethyl piperidine-g-PSSI)	1.25	5
HALS-4 (4-amino-2,2,6,6-tetramethyl piperidine-g-PSSI)	0.41	3

perature was kept at 0°C. Ethyl chloroformate (14.3 g, 0.1318 mol) in 30 mL of THF was added dropwise over 30 min, and the mixture was kept at 0°C for 1 h. Sodium azide (9.8 g, 0.1507 mol) was added over 120 mL of water over 30 min and stirred at 0°C for 1.5 h. Water (600 mL) was added dropwise, and the mixture was gradually allowed to attain the ambient temperature. The white solid that separated out was filtered, washed with water, recrystallized from ethanol (mp = 86°C, yield = 66.5%), and characterized [Fig. 1(a,b)]:



The polymer was characterized with $^1\text{H-NMR}$ and FTIR (Fig. 2). The IR spectrum showed the characteristic peak of isocyanate at 2266 cm^{-1} and the absence of a carbamate peak at 1745 cm^{-1} . The molecular weight data are given in Table I.

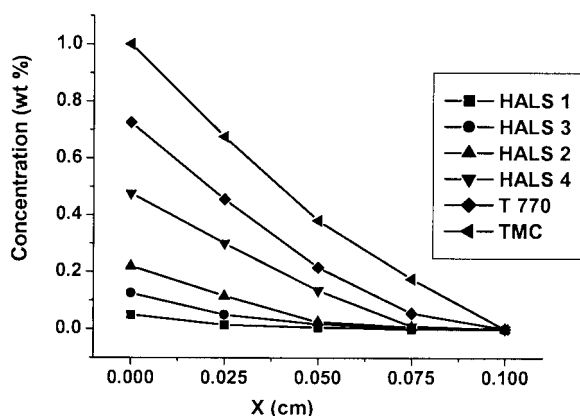


Figure 5 Concentration distribution of TMC, Tinuvin 770, HALS-1, HALS-2, and HALS-3 in HIPS-II films.

Step II: Synthesis of PSSI¹⁶ In a three-necked flask (4.4 mL, 0.027 mol), distilled styrene in 15 mL of toluene was placed, and 7 mg (0.0426 mmol) of AIBN and 0.521 g (0.003 mol) of cinnamoyl azide were added. A condenser with a guard tube was attached to the flask. The content of the flask was heated at 90°C at 24 h under a nitrogen flow. The flask was cooled, and the contents were poured into petroleum ether for the precipitation of the copolymer. The copolymer obtained was purified by dissolution in methyl ethyl ketone, and this was followed by precipitation in ethanol. The colorless product was dried at 60°C *in vacuo* (yield = 1.4 g):

Synthesis of polymeric 2,2,6,6-tetramethyl-4-piperidinol (HALS-1 and HALS-2)

The copolymer (PSSI; 0.5 g), 0.2 g of 2,2,6,6-tetramethyl piperidinol, and 1 mL (1 wt % solution in toluene) of dibutyl tin dilaurate were dissolved in 20 mL of dry toluene in a 100-mL flask and refluxed for 5 h at 80°C. The product was precipitated in ethanol, purified, and dried at 80°C *in vacuo*. The product was characterized by $^1\text{H}/^{13}\text{C-NMR}$ and FTIR (Fig. 3). The IR spectrum showed a characteristic band of ester (COO^-) at 1723 cm^{-1} :

TABLE III
D and S Values of TMC, Tinuvin 770, and Polymeric HALS in HIPS-II

Additive	$D \times 10^{-10}$ ($\text{cm}^2\text{ s}^{-1}$)	S (wt %)
TMC	30.0	1.2
Tinuvin 770	26.7	1.0
HALS-1	5.2	0.03
HALS-2	11.0	0.06
HALS-3	10.0	0.05
HALS-4	18.0	0.08

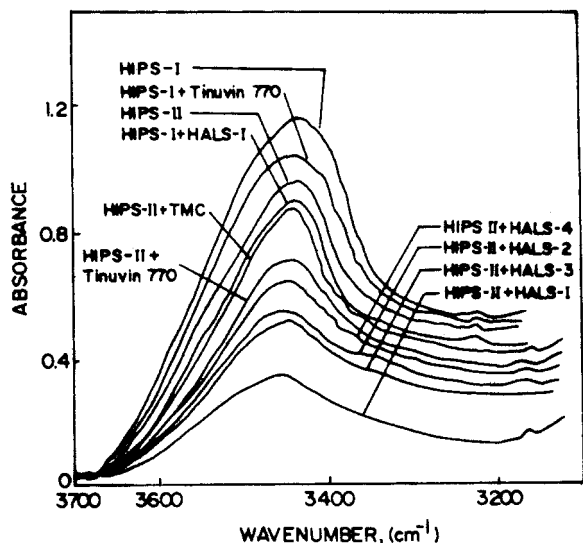


Figure 6 Evolution of the hydroxyl absorbance versus the wave number in 150-h-irradiated HIPS-1 and HIPS-II with various light stabilizers at 0.5 wt % concentrations.

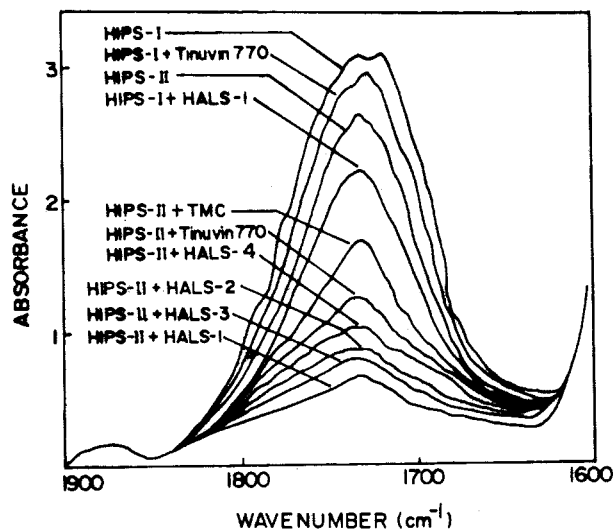
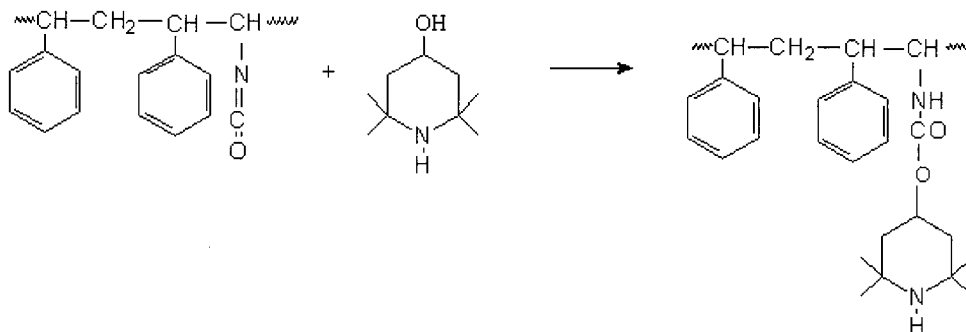
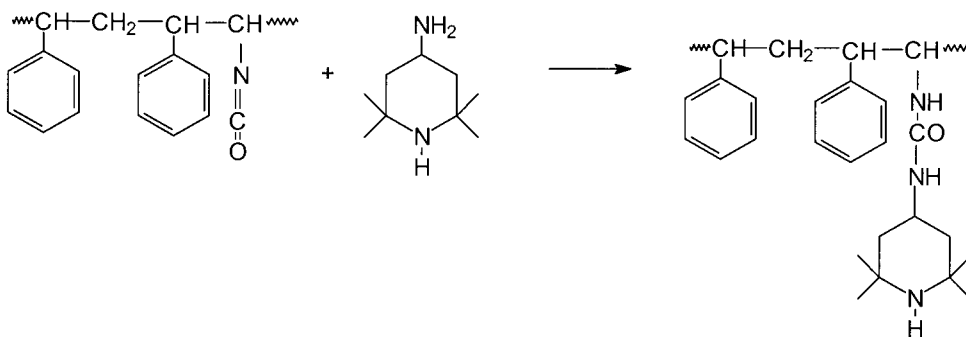


Figure 7 Plot of the difference in the carbonyl absorbance (ΔA) versus the wave number in 150-h-irradiated HIPS-1 and HIPS-II with various light stabilizers at 0.5 wt % concentrations.



Synthesis of polymeric 4-amino-2,2,6,6-tetramethyl piperidine (HALS-3 and HALS-4)

The copolymer was dissolved in 20 mL of dry toluene and refluxed with 0.1 mL of 4-amino-2,2,6,6-tetramethyl piperidine at 80°C for 5 h. The product was



filtered and washed with ethanol. It was then washed with petroleum ether and dried at 80°C *in vacuo*. The product was characterized by ¹H/¹³C-NMR and FTIR (Fig. 4). The spectrum showed a strong peak at 1745 cm⁻¹ corresponding to the carbamate group:

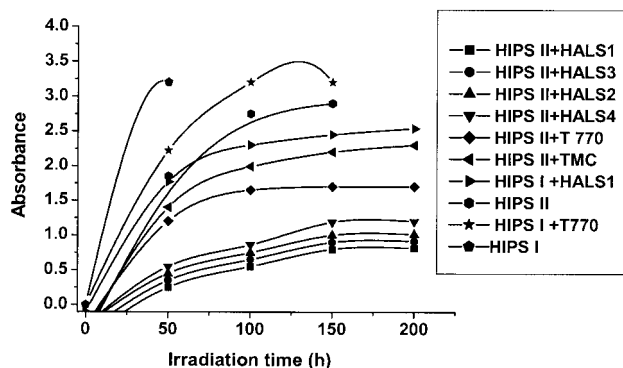


Figure 8 Rate of the carbonyl group formation with the irradiation time in HIPS-II films in the presence of various light stabilizers at 0.5 wt % concentrations.

Grafting determination

The HALS-g-PSSI film was Soxhlet-extracted in methanol for 6 h and then dried *in vacuo*. The weight percentage of the grafting was calculated as follows:

$$\text{Grafting (wt\%)} = (W_w - W_0) \times 100/W_0 \quad (1)$$

where W_w is the net weight of the HALS-g-PSSI film and W_0 is the initial weight of the film (Table II).

Mixing of the stabilizers

Different concentrations (0.2–1.0 wt %) of conventional HALSs (2,2,6,6-tetramethyl- μ -piperidinol (TMC) and Tinuvin 770) and polymeric HALSs (HALS-1, HALS-2, HALS-3, and HALS-4) were mixed with additive-free HIPS-I (3.1 wt % PB) and HIPS-II (7.9 wt % PB)¹⁷ by melt blending in a Minimax mixer (CSI-183

MMX, Custom Scientific Instruments, Cedar Knolls, NJ) at 180°C for 3 min and then were extruded.

Diffusion measurements

The diffusion measurement were carried out with a system described by Roe et al.¹⁸

A stack of 30 additive-free polymer films ($\sim 70 \mu\text{m}$) was placed between the additive sources ($\sim 200 \mu\text{m}$). The additives (2 wt %) were melt-blended in HIPS-II at 250°C for 2 min. These air-bubble-free additive films were kept at the bottom of the film stack. The films were kept in a vacuum oven at a constant temperature (TMC and Tinuvin 770 at 80°C for 150 h and HALS-1, HALS-2, HALS-3, and HALS-4 at 80°C for 150 h). The calibration was performed with a neat HIPS-II film, and the additive concentration was determined in a dimethyl sulfoxide solution at 264 nm by UV spectroscopy. To avoid errors caused by the additive adsorbed on the surface in contact with the additive source, we did not use the concentration of the film next to the additive source in our calculations.

The diffusion coefficient (D) was determined with the principle given by Moisan.^{10,19} 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 (c) is 0 at any distance from the additive source ($x > 0$), and that during the experiment ($t > 0$), c in the additive source ($x \leq 0$) remains constant and equals the solubility coefficient (S). c at position x and time t can be described as follows:

$$c(x,t) = S[1 - \text{erf}(x/K)] \quad (2)$$

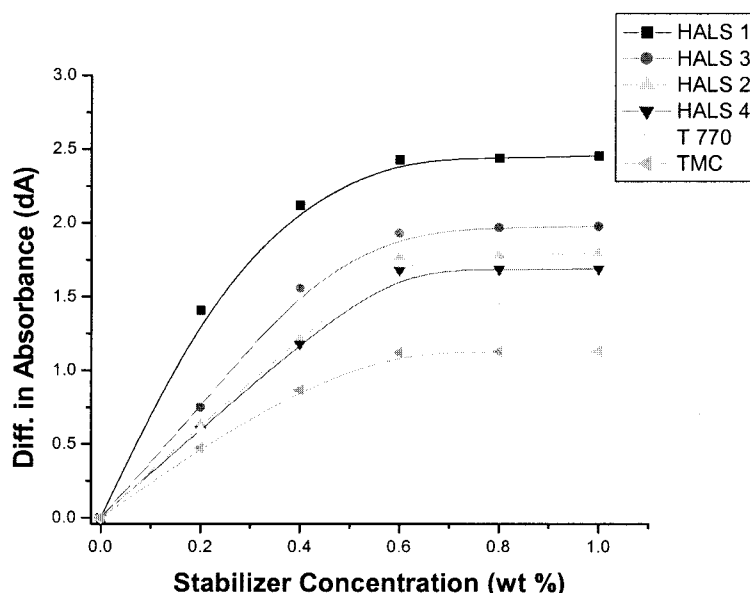


Figure 9 Plot of the difference in the carbonyl absorbance (ΔA) versus various stabilizer concentrations in HIPS-II after 200 h of irradiation.

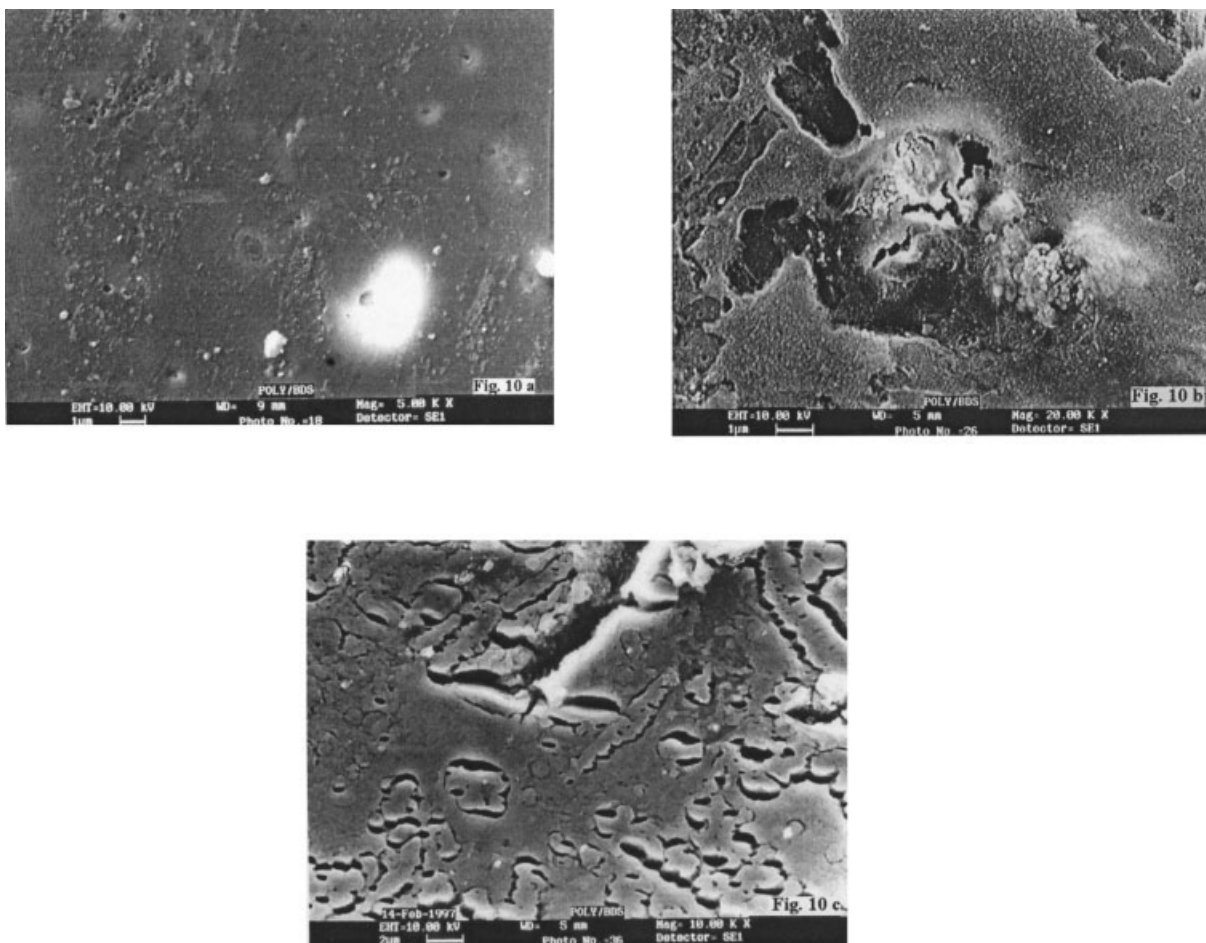


Figure 10 SEM photographs of photooxidized neat HIPS-II after 100 h of UV exposure at various magnifications: (a) 5000 \times , (b) 20,000 \times , and (c) 10,000 \times .

where K is determined by the time. D can be obtained as follows:

$$K = 2\sqrt{Dt} \quad (3)$$

For the calculation of D and S from the concentration profile, an interactive least-square curve-fitting program was used.

RESULTS AND DISCUSSION

We designed the polymeric HALSs by grafting them onto a synthesized copolymer (PSSI) with two criteria: (1) a sufficiently high molecular weight so that they did not easily diffuse out of the polymer (poor mobility) and (2) a high compatibility with the polymer so that the stabilizer could be dispersed uniformly in the polymer. These two aspects become particularly relevant for a multiphase polymer such as HIPS in which stabilizers can partition the different phases in the system. The synthesized HALS-*g*-PSSI copolymers were characterized by FTIR and $^1\text{H}/^{13}\text{C}$ -NMR spectroscopy. 2,2,6,6-Tetramethyl-4-piperidinol-*g*-PSSI (HALS-1 and HALS-2) showed characteristic peaks at 1723 cm^{-1} for ester

($-\text{COO}^-$). HALS-1 showed its peaks at 4.02 ppm (δ -bond; $\text{CH}-\text{NH}-\text{COO}^-$) in ^1H -NMR (Fig. 3) and at 174 ppm for ester carbon and at 120–128 ppm for the aromatic region. 4-Amino-2,2,6,6-tetramethyl piperidine-*g*-PSSI (HALS-3 and HALS-4) also showed characteristic bands at 1680 cm^{-1} for amide ($-\text{CONH}-$) and at 1745 cm^{-1} for carbamate ($-\text{NH}-\text{CO}-\text{NH}-$). In ^{13}C -NMR spectra of HALS-3, peaks were observed at 177 ppm for amide carbon ($-\text{CONH}-$) and at 120–128 ppm for the aromatic region (Fig. 4).

Performance evaluation of polymeric HALSs in HIPS

Figure 5 shows concentration profiles of TMC, Tinuvin 770, HALS-1, HALS-2, HALS-3, and HALS-4 in a film stack of HIPS-II after 150 h at 80°C. There was a very good fit between the experimental data and the theoretical curves obtained from eq. (2). The solubility of the additive was determined by extrapolation. D and S , calculated from the plots, are shown in Table III. In HALSs, D was $5\text{--}18 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, and S was 0.03–0.08 wt %, about 5–1.5 times lower than that of Tinuvin 770. This was due to the higher molecular

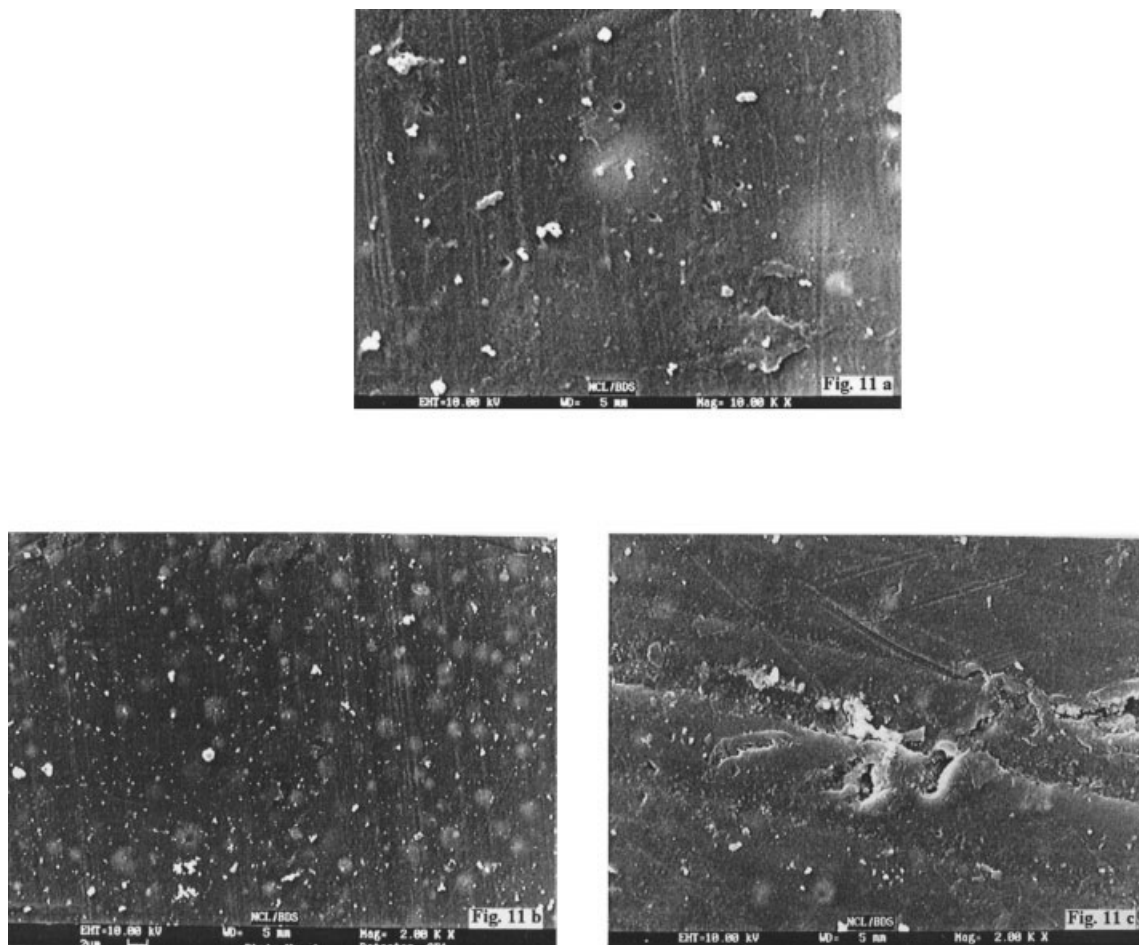


Figure 11 SEM photographs of HIPS-II with Tinuvin 770: (a) 75 h of UV exposure, (b) 75 h of UV exposure (magnification, 2000 \times), and (c) 150 h of UV exposure.

weight of the former, which restricted additive diffusion and solubility. D and S for an additive were reduced with an increase in the molecular weight and depended on the difference between the polarity of the polymer molecule and that of the additive.

The performance of conventional and polymeric HALSs in HIPS-II is plotted in Figures 6 and 7. The photoefficiency of the stabilizers was estimated by the measurement of the increments of the hydroxyl (3200–3700 cm^{-1}) and carbonyl (1620–1850 cm^{-1}) absorbance (ΔA). The neat film showed maximum hydroxyl (3420 cm^{-1}) and carbonyl (1723 cm^{-1}) absorptions at 150 h of UV exposure. The neat HIPS-I showed more rapid photodegradation than HIPS-II because of the smaller PB content (3.1 wt % PB), and it acted more or less as pure PS. Among the aged HIPS-II films containing stabilizers, ΔA was maximum with TMC and minimum with HALS-1. The polymeric HALSs were amorphous in nature and highly compatible with the polymer backbone; therefore, they were well dispersed in the polymer matrix and gave better stabilization. The greater stabilizing efficiency of HALS-1 over that of HALS-3 was due to the higher content of HALS (2.26 wt %) in the former.

The carbonyl group formation in the stabilized HIPS-II upon photoirradiation is shown in Figure 8. Unprotected HIPS-I showed a rapid increase in the carbonyl absorption increment just after 10 (HIPS-I) and 20 h (HIPS-II) of irradiation. HIPS-II stabilized with polymeric HALSs (0.5 wt %) showed remarkable photostability in comparison with HIPS-II stabilized with TMC and Tinuvin 770. In the case of a conventional stabilizer, a carbonyl absorption value of 0.1 was reached within 30 h of irradiation, whereas for an HALS-1-stabilized sample, there was no significant carbonyl group absorbance up to 50 h; with a longer irradiation time, a slow increase in the carbonyl absorbance was observed. The increase in the carbonyl absorbance (ΔA) was almost linear in polymeric HALS-stabilized samples, whereas for TMC- and Tinuvin 770-stabilized samples, the increase was nearly exponential. This could be explained by the fact that low-molecular-weight TMC and Tinuvin 770 underwent migration and leaching from the surface at longer irradiation times, whereas polymeric HALSs showed negligible diffusion and solubility in HIPS-II because of the high molecular weight and polar nature of the backbone of the polymer, consequently remain-

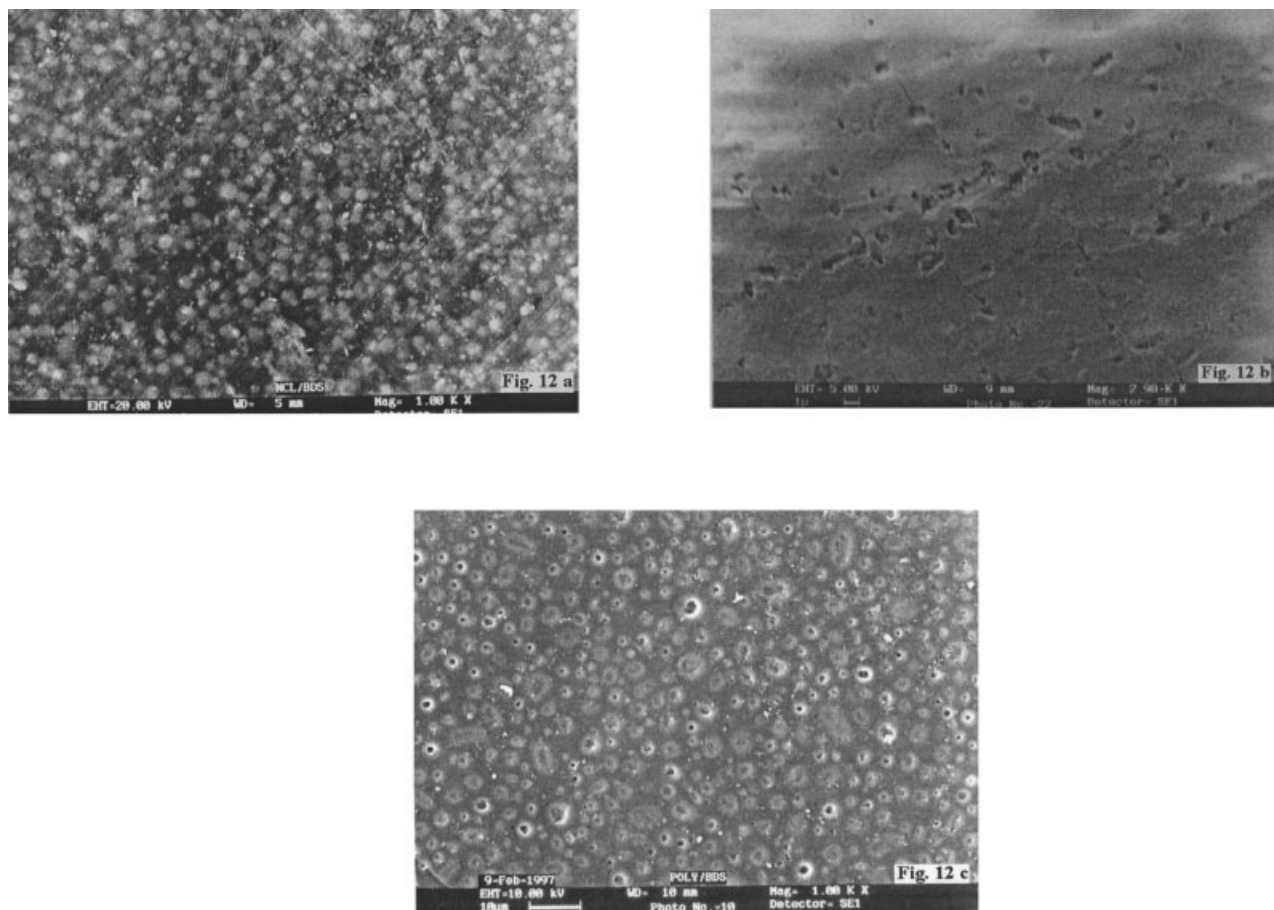
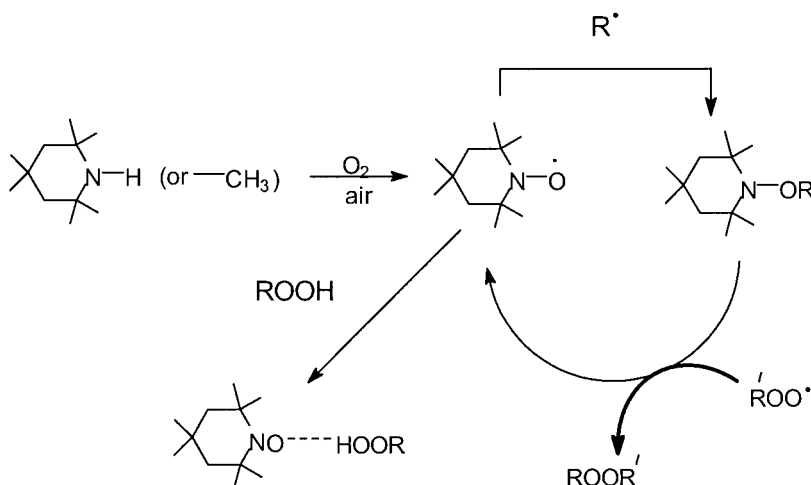


Figure 12 SEM micrographs of polymeric HALS-1: (a) 100 h of UV exposure, (b) 200 h of UV exposure (magnification, 2980 \times), and (c) 200 h of UV exposure (magnification, 1000 \times).

ing in the polymer for a long enough time to be able to exert their stabilizing behavior.

HALS-1 and HALS-2 had a better effect on the photostability than HALS-3 and HALS-4, respectively, in all cases. Shylapinthok et al.²⁰ reported that, if the

—NH group is not fully hindered as in HALS-3 and HALS-4, the photostabilizing efficiency is considerably reduced. Moreover, HALS-1 and HALS-2 had higher molecular weights than HALS-3 and HALS-4, respectively, because nitroxyl radicals



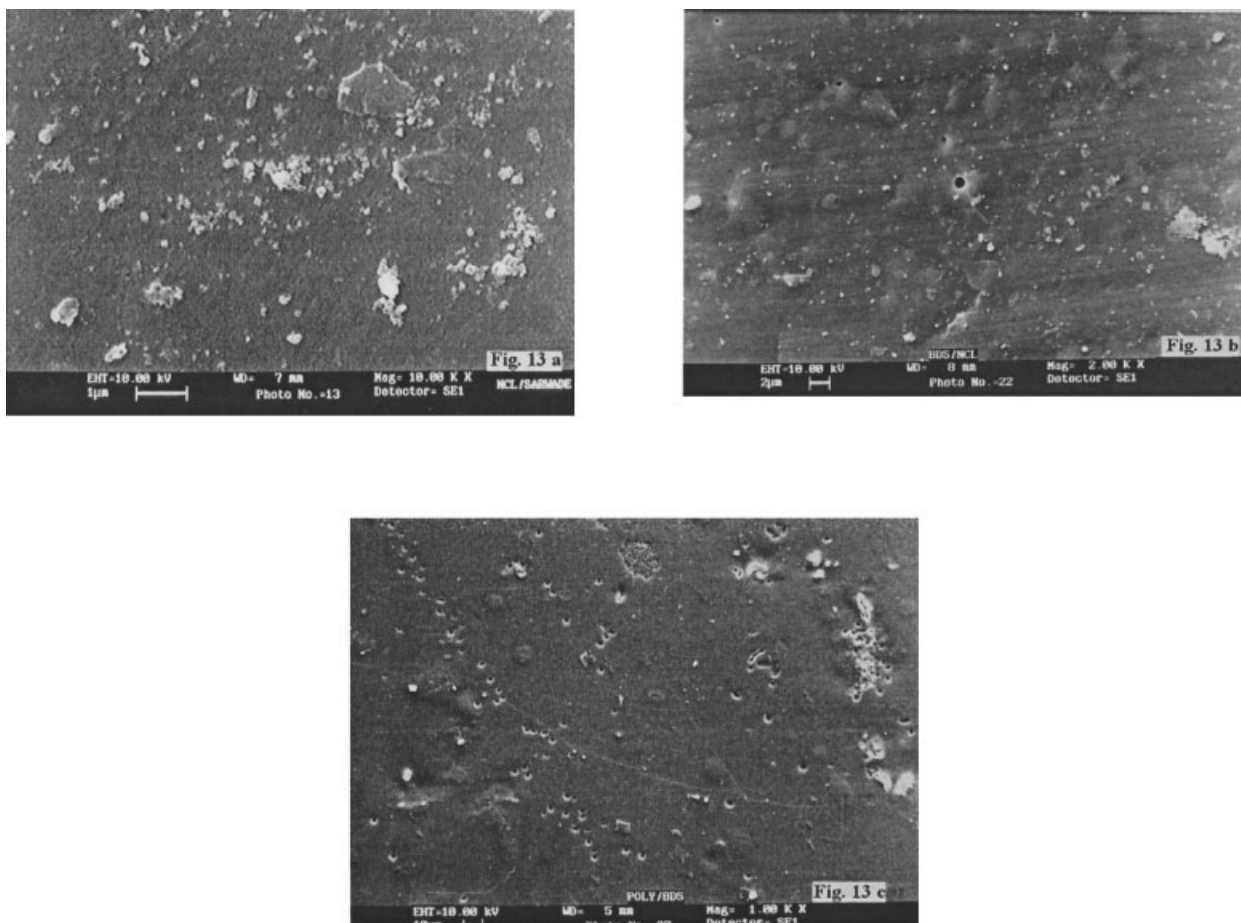


Figure 13 SEM micrographs of polymeric HALS-3: (a) 100 h of UV exposure, (b) 200 h of UV exposure (magnification, 2000 \times), and (c) 200 h of UV exposure (magnification, 1000 \times).

are efficient scavengers, hydroperoxide decomposers, and traps for macroradicals, which are produced during oxidative degradation.

It has been postulated that nitroxyl radicals are regenerated in the process and are the main active species in the stabilization. However, all the polymeric HALSs showed remarkable photostability;^{21,22} HALS-4 had the poorest compatibility (low molecular weight and HALS content), with the matrix limiting its diffusivity, and HALS-1 had the highest compatibility and, therefore, the highest diffusivity.

It is generally believed that for any appreciable stabilizing action, the stabilizer should be present in a sufficient concentration and up to a reasonable depth.^{19,23} The 1.0 wt % concentrations of the conventional stabilizers (TMC and Tinuvin 770) and 0.5–0.8 wt % concentrations of the polymeric HALSs (HALS-1, 0.5 wt %; HALS-2, 0.7 wt %; HALS-3, 0.6 wt %; and HALS-4, 0.8 wt %) were the optimum concentrations as a saturation limit in the photostabilization of HIPS-II was reached at these concentrations (Fig. 9); after that, no change in absorbance was observed with a further increase in the stabilizer concentrations.

The differences in the effectiveness of the conventional stabilizers and polymeric HALSs, as a function

of the stabilizer concentration, were indicative of the important roles played by the ability of the polymeric stabilizer in the matrix and the higher degree of compatibility, which resulted in higher solubility and greater diffusivity. This also enabled the polymeric HALSs to distribute themselves evenly throughout the matrix.

Morphological changes

The 100-h-exposed neat HIPS-II film (Fig. 10) showed microcavities on the surface. This was due to chain scission that initially occurred on the surface. Figure 11 shows SEM photographs of HIPS-II with Tinuvin 770, which was well dispersed in the matrix. The irradiated (75 and 150 h) films showed microcavities and cracks on the surface. HALS-1 was evenly dispersed (Fig. 12) throughout the polymer matrix. This additive had better compatibility with the HIPS matrix and was grafted onto the PS phase. The 100- and 200-h-photooxidized films showed microcavities on the surface. The microcracks were not observed in the stabilized films for longer irradiation times, whereas the neat film showed microcracks. Figure 13 shows SEM photographs with HALS-3. Phase separation was

observed in the film. The stabilizer particles were dispersed throughout the film. This indicated that HALS-3 was not as compatible with the polymer matrix as HALS-1. The 75-h-exposed film showed microcavity initiation on the film surface.

CONCLUSIONS

Heterophasic HIPS films were more effectively protected against photoirradiation by polymeric HALSs than commercial low-molecular-weight HALSs. The improved photostability of such materials was attributed to the high-molecular-weight, amorphous nature of the additives and stabilizers and better compatibility between the additive and polymer.

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