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A new polymeric HALS: preparation of an addition polymer of DGEBA–HALS and its photostabilizing effect

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Abstract

A linear epoxide–amine type of a new polymeric HALS was prepared by an addition polymerization of 2,2-bis(4-glycidyloxyphenyl)-propane and 4-amino-2,2,6,6-tetramethylpiperidine (ATMP) in chlorobenzene. Two types of addition polymers, high molecular weight HALS (HMH) and low molecular weight HALS (LMH) were isolated by precipitation in acetone. The structure of HMH was characterized from the NMR and MALDI-TOF spectra. The effects of the reaction conditions on the yield of HMH and LMH were observed by varying the reaction conditions such as monomer concentration, reaction temperature, and reaction time. The yield of HMH increased with the amount of the ATMP concentration, reaction temperature, and reaction time. HMH is fairly miscible with polypropylene (PP), polystyrene (PS), and styrene–butadiene rubber. The photostabilizing effect of HMH on the photooxidation of PP and PS at 254 or 310 nm was studied from the UV and IR absorption spectral changes. The results indicate that the photostabilization effect of HMH was similar to or better than that of Cyabsorb UV-3529, a commercially available polymeric HALS. © 2002 Published by Elsevier Science Ltd.

Keywords: Photostabilizer; Polymeric hindered amine light stabilizers; Epoxide–amine addition polymer

1. Introduction

Polymeric materials exposed to sunlight undergo photodegradation resulting in the discoloration, cracking of surface, stiffening, and decrease in the mechanical properties. Light stabilizers should be added to outdoor polymeric products in order to minimize such unwanted effects of the sunlight. Hindered amine light stabilizers (HALS) are one of the most effective photostabilizers for polymers and have been used in a large number of commercial polymers. They are efficient and cost-effective in many applications, despite their high prices. However, low molecular weight HALS (LMH) vaporizes easily, emitting harmful amines, and have poor extraction resistance, decreasing their photostabilization effect. They also decompose during processing and migrate within the polymers, resulting in deposition on the polymer surfaces. These drawbacks caused by the low molecular HALS can overcome through the use of the polymeric HALS [1,2].

The polymeric stabilizers bring a higher thermal stability, more resistance to extraction, and lower toxicity. Various kinds of polymeric HALS were prepared and commercialized. They are obtained by copolymerization or homopolymerization of vinyl monomers containing a HALS group [3–5]. Other polymeric HALS such as Tinuvin-662 and Chimassorb-994 are obtained by polycondensation polymerization [6,7]. Alternatively, many polymeric HALS can be prepared through functionalization of preformed polymers [8–10]. In addition to polymerization, oligomeric HALS can be prepared through simple reactions of multifunctional organic compounds [6,11,12]. Although much development has progressed in the light stabilization of polymeric materials, the stabilization efficiency of the polymeric HALS has not been overcome in many applications until now. Therefore, polymeric photostabilizers suitable for various polymeric systems should be developed in order to optimize their photostabilization efficiency.

The efficiency of the polymer additives was affected mainly by the diffusion rate and homogeneity of the additives in the polymer matrix. Comparing with the low molecular weight additives, it is very likely that the efficiency of the high molecular weight additives decreased due to its low diffusion rate. Furthermore, an increase in the molecular weight of the polymer additive results in the

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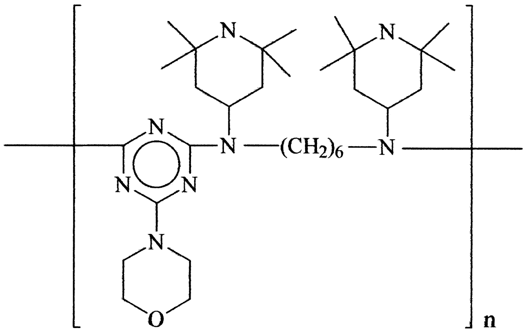


Cyabsorb UV-3529

Scheme 1.

decrease in miscibility between the additive and polymer matrix. Thus, in order to distribute a polymer additive into the polymer matrix evenly, the molecular weight of the additive and miscibility between the additive and polymer are very important factor. It was reported that the optimum molecular weight for the polymeric HALS is less than 3000 [1].

On the other hand, network polymers have been obtained by the addition polymerization of epoxide with amine. They have been used as adhesives, composites and laminates due to their excellent mechanical, thermal and electrical properties. The preparation of linear epoxide–amine addition polymers has been considered to be impractical due to their cross-linking reactions. However, high molecular weight linear epoxide–amine addition polymers have been developed by Klee et al. [13–16]. For the preparation of linear epoxide–amine polymers, special reactions must be accomplished such as high purity, stoichiometry of monomers, and a reaction near the glass transition temperature at 120–130 °C [15,16].

In the previous studies, we reported on the preparation of the polymeric HALS containing maleimide groups and their photostabilization effects on polystyrene (PS) or styrene–butadiene rubber (SBR) [17,18]. The present paper deals with the preparation of a new type of polymeric HALS based on the linear epoxide–amine addition polymerization and its effects on the photooxidation of polypropylene (PP) and PS. The polymeric HALS prepared in this experiment has moderate molecular weight ($\bar{M}_n = 2400$) and was fairly miscible with various polymers such as PP, PS, and SBR with a good photostabilizing efficiency comparable to Cyabsorb UV-3529 (Scheme 1), a commercially available polymeric HALS.

2. Experimental section

2.1. Materials

2,2-Bis(4-glycidyloxyphenyl)propane (DGEBA) and 4-amino-2,2,6,6-tetramethyl-piperidine (ATMP) were purchased from Tokyo Kasei Chemical Company and used as received. PP (CY-120, melt flow index = 1.0 g/10 min) was obtained from Honam Petrochemical Co. and purified by precipitation from toluene solution into methanol. SBR (SBR-1502, $\bar{M}_n = 485,000$) and PS (general purpose PS HF-2660, $\bar{M}_n = 310,000$, dispersity = 5.8) were obtained from Japan Synthetic Rubber and Samsung Co., respectively, and used after purification by precipitation from THF polymer solution into methanol. Cyabsorb UV-3529 ($\bar{M}_w =$ 1700) was obtained from Needfill Co. and used without further purification.

2.2. Instruments

Ultra-violet (UV) spectra were taken on a Jasco model V-530 spectrophotometer. Infrared (IR) spectra were obtained with the use of a Shimadzu model FTIR-8300 spectrophotometer. ^{1}H nuclear magnetic resonance spectra were recorded on a Bruker 300 MHz NMR spectrometer. MALDI-TOF spectrum was obtained from a Kratos model Kompact MALDI II mass spectrometer. Differential scanning calorimetry measurements were carried out with a Dupont model 910 thermal analyzer under N_2 atmosphere at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) was carried out with a Young-in model 910 solvent delivery module equipped with a Young-Lin M720 absorbance detector. A Shimadzu HSG-15 GPC column was used for the measurement of molecular weight determination. Molecular weight was calibrated using the PS standards. A Mini–max molder (Bau-Technology Ba-915) and a heating press (Claver Laboratory, USA) were used to prepare the films for the compatibility experiments. Irradiations were carried out in a Rayonet photochemical reactor (The Southern New England UV company model 208) equipped with 254 or 310 nm fluorescent lamps. One module of the photochemical reactor was placed in a horizontal position and irradiated. The light intensity measured by a radiometer (Vilber Lourmat Co., model VLX-3W) was 3.83 mW/cm^2 at 254 nm and 0.97 mW/cm^2 at 310 nm.

2.3. Preparation of polymeric HALS

A typical procedure for the preparation of the DGEBA–HALS addition polymer is as follows: DGEBA (12.06 g, 35.4 mmol) and ATMP (5.54 g, 35.4 mmol) were dissolved in chlorobenzene (31.8 ml, 200 wt%) and refluxed at 120 °C for 72 h. After the addition of a small amount of THF to reduce viscosity, the resulting polymer was isolated by precipitation into ethyl ether (1150 ml) and purified by reprecipitation from the THF polymer solution (57 ml) into ethyl ether (1150 ml) (Yield 12.3 g, 70%).

The obtained DGEBA–HALS addition polymer was further separated by precipitating it in acetone (860 ml). High molecular weight HALS (HMH), the insoluble part of the addition polymer in acetone (viscous product), was dissolved in THF and isolated by precipitation in ethyl ether. LMH, the soluble part of the addition polymer in acetone, was obtained by evaporation of the solvent. The isolated polymers were dried in vacuum at 60 °C for 4 h. Yield of HMH was 11.7 g (95%) and that of LMH was 0.6 g (5%) in the 12.3 g of the addition polymer.

HMH, IR (KBr pellet, cm^{-1}): 3380 (–OH), 3035, 2966 (C–H), 1604, 1508 (benzene ring), 1249 (C=O), 1037, 829. ^{1}H NMR ($CDCl_3$, 300 MHz); δ (ppm) = 7.03–7.14, 6.84–6.7 (d, phenyl), 3.9–4.1 (–O–CH_2–) 3.7–3.8 (m, –NH), 2.6–3.0 (broad, –CH_2–, –N–CH<, –CH(OH)–), 2.17 (s, C–NH–C), 1.8–1.9 (m, –OH), 1.60 (s, CH_3–C–CH_3), 1.0–1.1, 1.17 (m, –CH_3 and –CH_2–N–CH_2– in ATMP moiety). LMH, IR (KBr pellet, cm^{-1}): 3380 (–OH), 3035, 2966 (C–H), 1604, 1508 (benzene ring), 1249 (C=O), 1037, 829.

2.4. Determination of HMH and LMH content

The content of HMH and LMH in the addition polymer was determined at various reaction conditions. Typically, an equimolar amount of DGEBA (2.1 g, 6.29 mmol) and ATMP (0.98 g, 6.2 mmol) was dissolved in chlorobenzene (2.9–19.6 ml), and refluxed for 4–72 h at the temperature range of 80–130 °C. The addition polymer was isolated by double precipitation in 200 ml of diethyl ether. HMH and LMH were separated by precipitating the addition polymer from THF solution (10 ml) into acetone (150 ml). The wt% of HMH and LMH in the addition polymer was determined after isolation by the same procedure as described above.

2.5. Compatibility of HMH

The compatibility of HMH with PP, PS, or SBR was observed from the transparency of the polymer film after addition of 1–10 wt% of HMH. The PP film containing HMH was prepared by mixing PP and HMH in the Mini–max molder at 180 °C for 10 min followed by pressing 15,000 pounds for 5 min at 180 °C in the heating press. A mixture of PS and HMH were prepared by dissolving PS and 10 wt% HMH in THF followed by precipitation from THF solution into methanol. The PS film containing HMH was prepared by pressing 15,000 pounds for 5 min at 180 °C in the heating press. A SBR film containing 10 wt% HMH was prepared by spin coating method after dissolving SBR and HMH in THF.

UV transmission spectra of the polymeric HALS were observed after dissolving HMH (0.4 mg) or Cyabsorb UV-3529 (3.4 mg) in methanol (10 ml).

2.6. Measurement of photostabilizing efficiency

The photostabilizing efficiency of HMH in PP or PS was monitored by the measurement of the carbonyl group changes from the IR absorption spectra and by the measurement of the UV absorption spectral changes at 240 and 280 nm upon irradiation with 254 or 310 nm UV light. The PP film containing polymeric HALS was prepared by the same procedure for the compatibility determination. A PS solution containing a polymeric HALS was prepared by dissolving PS (1.0 g) and 0.5–2.0 wt% of HMH or UV 3529 in THF (10 ml). The PS solution was cast on a KBr pellet and the film on the KBr pellet was dried for 2 h under reduced pressure at room temperature. IR absorption spectral changes of the film upon irradiation with 254 or 310 nm UV light were observed. The ratio of absorbance (A_t/A_0) at 1720 cm^{-1} from the IR spectra was calculated after normalization with the absorption band at 1490 cm^{-1} for the PS film and at 1458 cm^{-1} for the PP film to correct the film thickness.

3. Results and discussion

3.1. Characterization

Generally, the epoxide–amine addition polymers are not film-forming or convertible by thermal process due to their cross-linked structure. However, relatively low molecular weight linear polymers were obtained in solution polymerization of epoxide and amine [13]. It was expected that the linear addition polymers would be obtained by solution polymerization of DGEBA and ATMP. A linear structure of the addition polymer **3** as well as the polymer **1** which

Table 1
Preparation conditions and physical properties of the DGEBA–ATMP addition polymer

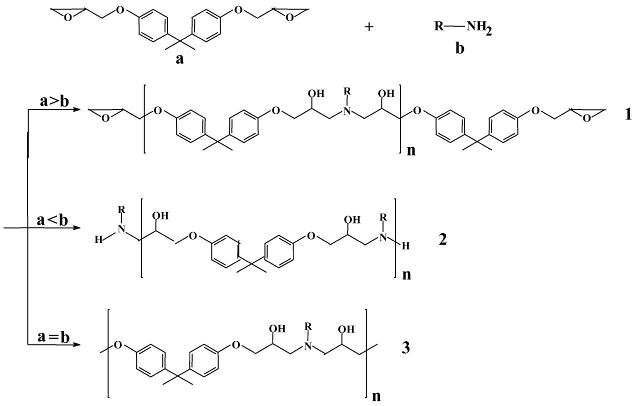
Monomer		Yield[a] (%)	Polymer distribution (%)	Polymer composition[b] (DGEBA/ATMP)	T_g (°C)	T_d (°C)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
DGEBA, g (mmol)	ATMP, g (mmol)							
2.0 (5.9)	0.92 (5.9)	70	HMH: 95	1:1	110	340	2400[c]	1.24
			LMH: 5	1:1	108	300	600[d]	–

[a] Polymerization was carried out with 9.24 mol% of ATMP at 120 °C for 24 h.

[b] Determined from 300 MHz NMR spectra in $CDCl_3$.

[c] GPC column, HSG-15; PS standards were used for the molecular weight determination.

[d] Determined from 300 MHz NMR spectrum using 3-bromopyridine as an internal standard in $CDCl_3$.



Scheme 2.

contains glycidyl end-groups, and the amino-terminated polymer **2** would be obtained as shown in Scheme 2 [13,14].

Polymerization was carried out in equimolar amount of DGEBA and ATMP in chlorobenzene at 80–130 °C. The addition polymer was isolated by precipitation in ethyl ether. HMH and LMH in the addition polymer were separated after precipitating in acetone [14]. Table 1 shows a summary of the typical reaction conditions and physical properties of the DGEBA–ATMP addition polymer. The over-all yield of the addition polymer was 70%. The addition polymer was a mixture of 95 wt% HMH and 5 wt% LMH. T_g of HMH and LMH was around 110 °C and the onset of thermal decomposition temperature of HMH and LMH was 340 and 300 °C, respectively.

HMH is soluble in THF, chlorobenzene, but insoluble in acetone, alcohol, chloroform, or ethyl ether. The average molecular weight of HMH determined by GPC was about 2400. Fig. 1 shows MALDI-TOF spectrum of HMH. It shows the formation of amino-terminated polymers **2** based on their molecular ions at m/z 652 ($n = 1$), 1149 ($n = 2$), 1646 ($n = 3$), 2143 ($n = 4$), 2639 ($n = 5$), 3136 ($n = 6$). Furthermore, as shown in Scheme 3, a cleavage of C–O bond in the polymer **2** results in the second series of fragment ions with M-213 at m/z 936 ($n = 2$), 1433 ($n = 3$), 1930 ($n = 4$), 2483 ($n = 5$). The most abundant polymer in HMH was polymer **2** with molecular weight of 1149 ($n = 2$). The polymer **1**, which contains glycidyl end-groups and the DGEBA–ATMP 1:1 addition polymer, **3** were not observed.

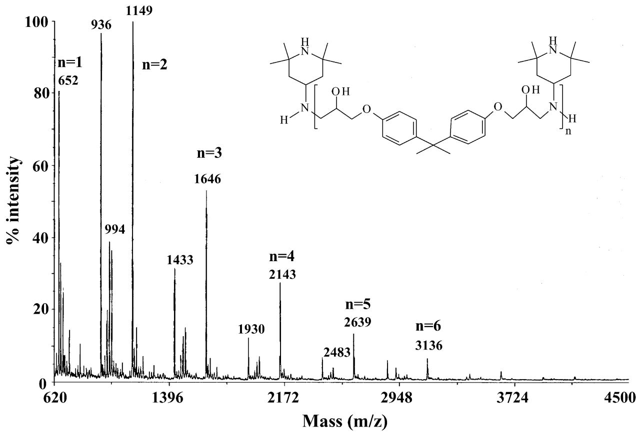
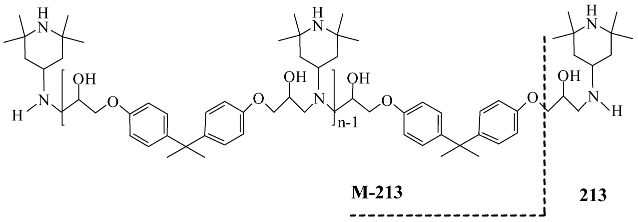


Fig. 1. MALDI-TOF spectrum of HMH.



Scheme 3.

LMH is soluble in THF, chlorobenzene, alcohol, chloroform, or acetone, but insoluble in ethyl ether. The NMR spectrum showed that LMH is 1:1 addition products of DGEBA and ATMP with low molecular weight. The molecular weight of LMH determined from NMR was about 600. Klee et al. [13,15] reported that a small amount of cyclic oligomers was found in linear epoxide–amine addition polymers which can be removed by precipitation in acetone [14]. The epoxy number of LMH was 0.15, which implies that LMH has no epoxy group. These results suggest

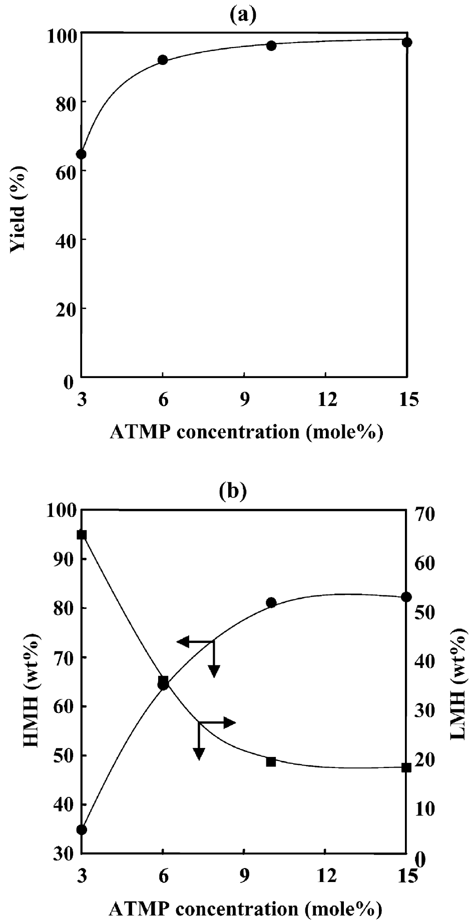


Fig. 2. Relationship between the ATMP concentration (a) with the yield of addition polymer, and (b) with the composition of the addition polymer. Polymerization was carried out at 120 °C for 24 h.

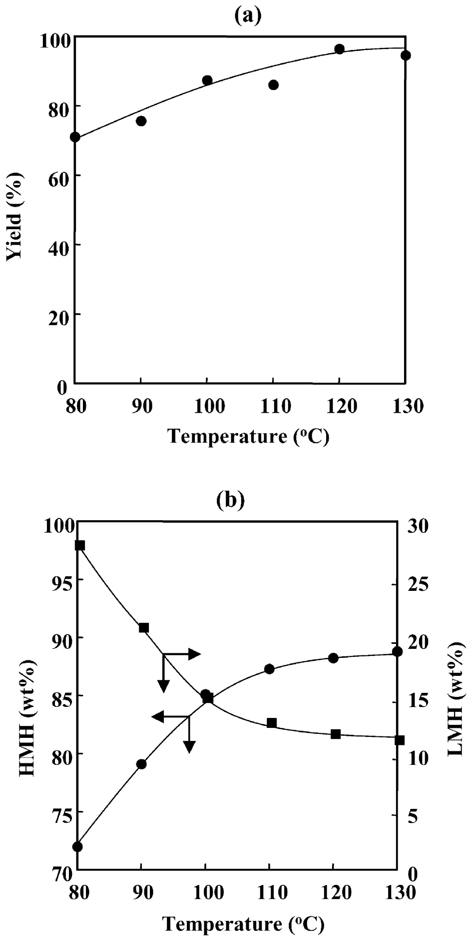


Fig. 3. (a) Effect of the reaction temperature on the yield of addition polymer, and (b) relationship between the polymer composition and reaction temperature. Polymerization was carried out with 9.24 mol% of ATMP over 24 h.

that LMH is a mixture of cyclic oligomers, but attempts to isolate them were unsuccessful.

3.2. Polymerization conditions

The molecular weight of the epoxide–amine addition polymer was affected by the reaction temperature, reaction time, concentration of the solvent, and precipitation solvent [16]. In order to study the effect of reaction conditions on the yield of HMH and LMH, experiments were carried out with varying reaction conditions.

Fig. 2(a) shows the yield of addition polymer as a function of ATMP concentration at constant reaction time (24 h) and temperature (120 °C). The yield of the addition polymer increased from 65 to 97% when the ATMP concentration changed from 3 to 15 mol%. Thus, an increase in the monomer concentration increases the yield of the addition polymer. Fig. 2(b) shows the composition of the addition polymer. The amount of HMH in the addition polymer increased from 35 to 83% with the increase in the ATMP concentration from 3 to 15 mol%, while that of LMH decreased from 65 to 20 wt%. These results indicate that the dilution of the monomer concentration increases the yield of LMH, while it decreases that of HMH.

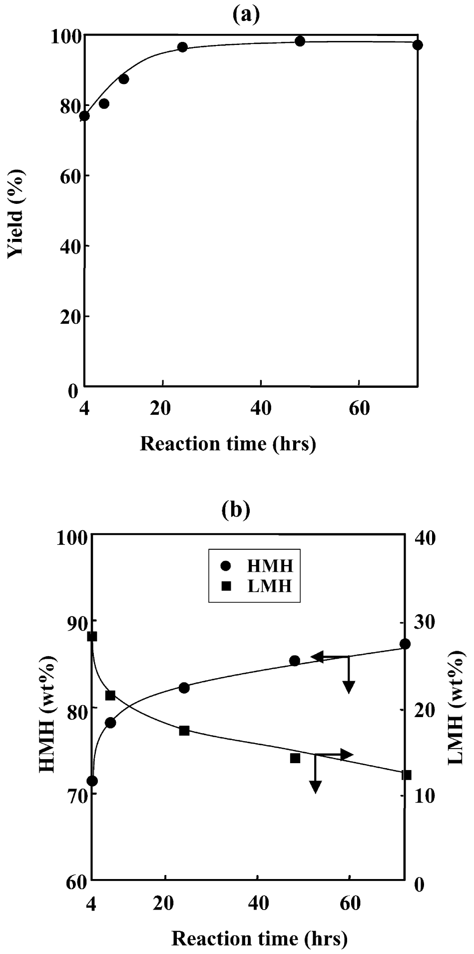


Fig. 4. (a) Effect of reaction time on the yield of addition polymer. (b) Relationship between the polymer composition and reaction time. Polymerization was carried out with 9.24 mol% of ATMP at 120 °C.

Fig. 3(a) shows the effect of the reaction temperature on the yield of the addition polymer at constant reaction time (24 h) and ATMP concentration (9.24 mol%). The yield of the addition polymer increased from 70% at 80 °C to 95% at 130 °C of reaction temperature. Fig. 3(b) shows the relationship between the polymer composition and reaction temperature. The amount of HMH in the addition polymer rose from 72 wt% at 80 °C to 88 wt% at 130 °C, while that of LMH fell from 28 wt% at 80 °C to 12 wt% at 130 °C. Thus, the formation of LMH was favorable at the low reaction temperature, while that of HMH decreased.

Fig. 4(a) shows the effect of reaction time on the yield of an addition polymer when polymerization was run at 120 °C with 9.24 mol% of ATMP. The yield of the addition polymer was 77 wt% at 4 h of reaction time, and it increased to 97 wt% at above 50 h. Fig. 4(b) shows the relationship between the polymer composition and reaction time. The amount of HMH in the addition polymer increased from 72 to 87 wt%, while that of LMH decreased from 28 to 13 wt%

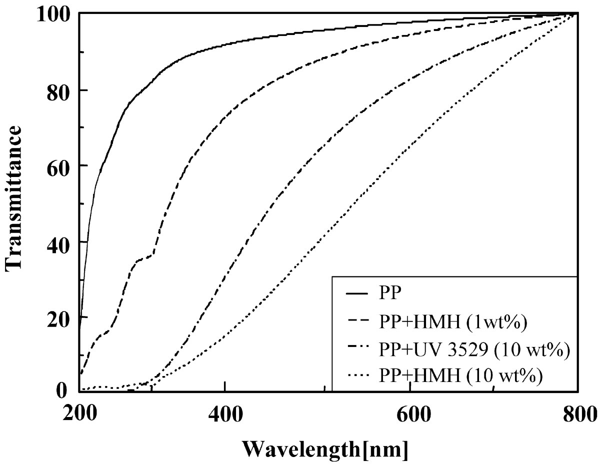


Fig. 5. UV–vis spectra of PP films containing HMH or Cyabsorb UV-3529.

at 4 and 72 h of reaction time, respectively. Thus, the increase of reaction time favors the formation of the addition polymer and HMH.

Experimental results show that yields of the addition polymer increased with an increase in the ATMP concentration, the reaction time, and reaction temperature. The formation of HMH was favorable at the high ATMP concentration, high reaction temperature, and long reaction time. The formation of HMH and LMH was most strongly affected by the ATMP concentration.

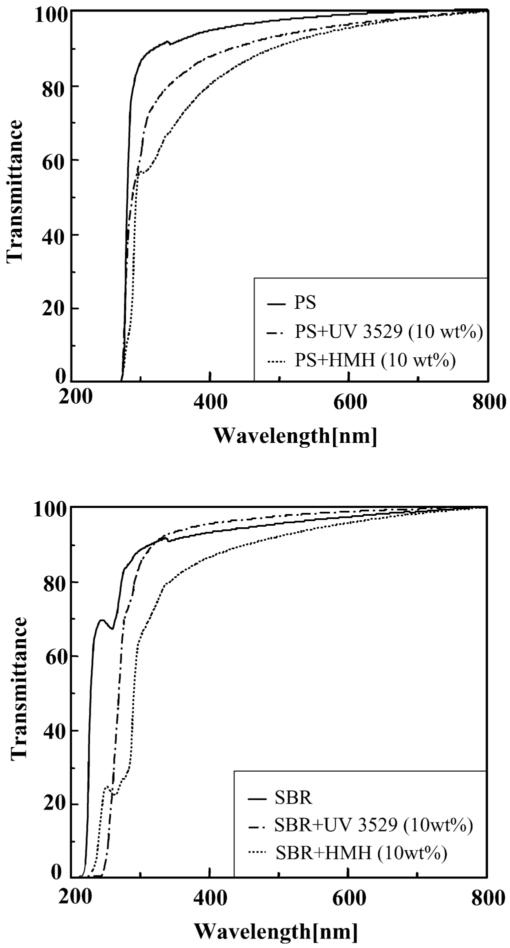


Fig. 6. UV–vis transmission spectra of PS and SBR films containing 10 wt% HMH or Cyabsorb UV-3529.

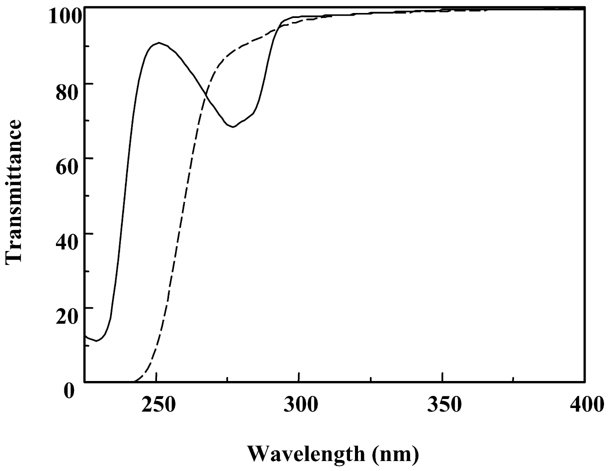


Fig. 7. UV–vis transmission spectra of HMH (—) and Cyabsorb UV-3529 (- - -) in methyl alcohol.

3.3. Compatibility

The compatibility of HMH with PP, PS, and SBR was observed from the transparency of the polymer film [19] after addition of 1–10 wt% HMH. The PP and PS film containing HMH was prepared by pressing the polymer and HMH mixture in the heating press. The SBR film containing HMH was prepared by spin coating method after dissolving SBR and HMH in THF.

Fig. 5 shows UV–vis spectra of PP films containing 0, 1, 10 wt% of HMH and 10 wt% of Cyabsorb UV-3529 with the film thickness of 50–55 μm. The PP film containing 10 wt% of HMH was more turbid than that containing 10 wt% of Cyabsorb UV-3529, but that containing 1 wt% of HMH was fairly transparent in the visible region. This result indicates that HMH is miscible with PP below 1 wt%.

Fig. 6 shows UV–vis spectra of the PS and SBR films containing 0 and 10 wt% of HMH or Cyabsorb UV-3529. Thickness of the PS and SBR films was about 60 and 18–19 μm, respectively. The result shows that the PS or SBR films containing 10 wt% of HMH have a good transparency compared to that containing 10 wt% of Cyabsorb UV-3529. This indicates that HMH is fairy compatible with PS and SBR up to 10 wt% of HMH.

The UV–vis spectra of the polymer films containing polymeric HALS show long absorption tailings up to 800 nm as shown in Figs. 5 and 6. In order to clarify whether absorption tailings are due to light scattering of the polymer film or absorption of polymeric HALS, UV–vis spectra of HMH and Cyabsorb UV-3529 in methanol were observed. As shown in Fig. 7, both the polymeric HALS have no

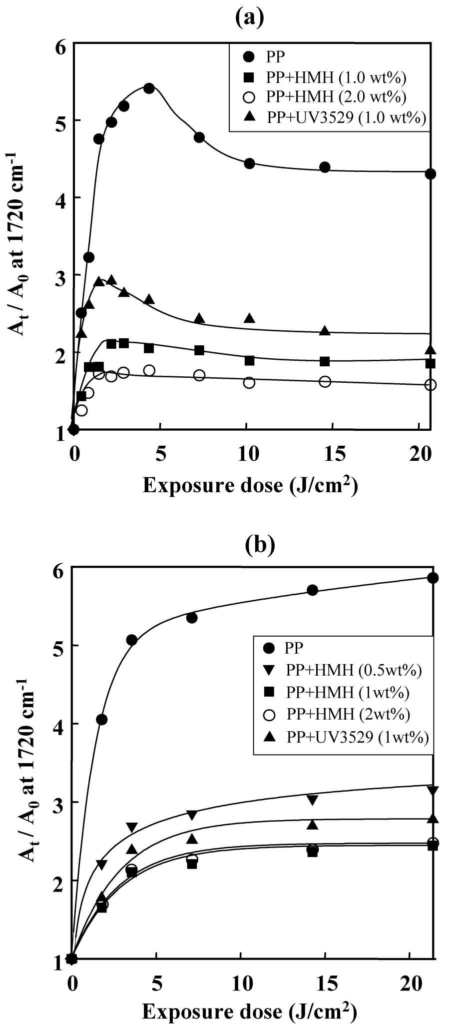


Fig. 8. Plot of A_t/A_0 of the PP films on a KBr pellet at 1720 cm^{-1} as a function of exposure dose. Irradiations were carried out with (a) 254 nm and (b) 310 nm UV light in air.

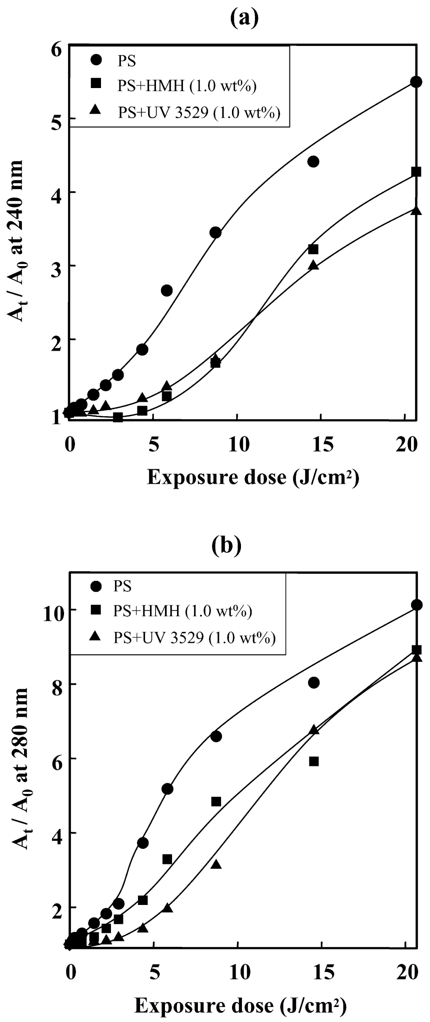


Fig. 9. Plot of A_t/A_0 of the PS films at (a) 240 nm and (b) 280 nm as a function of exposure dose. Irradiations were carried out with 254 nm UV light in air.

absorption above 375 nm. This indicates that absorption tailing of the polymer films containing polymeric HALS comes from the light scattering.

3.4. Photostabilization of PP and PS

The photostabilizing efficiency of HMH on the photooxidation of PP and PS was studied from the UV and IR absorption spectral changes, and the results were compared with that of Cyabsorb UV-3529.

Fig. 8 shows absorbance changes (A_t/A_0 at 1720 cm^{-1}) of PP films containing 1–2 wt% of HMH or 1 wt% UV 3529 as a function of exposure dose at (a) 254 nm and (b) 310 nm in an atmosphere of air. The absorbance changes of the PP films at 1720 cm^{-1} decreased with the amount of polymeric HALS, and the photooxidation of PP at 254 and 310 nm were decreased with the addition of polymeric HALS. The relative photostabilization efficiency of the polymeric HALS increased in the order of Cyabsorb UV 3529 (1 wt%) < HMH (1 wt%) < HMH (2 wt%) at 254 nm, and HMH (0.5 wt%) < Cyabsorb UV 3529 (1 wt%) < HMH (1 or 2 wt%) at 310 nm. This result indicates that the photostabilizing efficiency of HMH was greater than that of Cyabsorb UV 3529 at equal amount of the polymeric HALS.

UV absorption spectral changes of a PS film containing 10 wt% HMH upon irradiation with 254 nm UV light in the air show that all the absorbance in the UV region (<400 nm) increased with irradiation time, and the transparent PS film became slightly yellow with irradiation. This is due to the formation of various chromophoric groups such as polyene, acetophenone, and benzalacetophenone [20].

It is generally accepted that acetophenone end-groups are formed during UV irradiation of PS, and it is most probable that they are responsible for the yellow coloration of a polymer [20]. The formation of acetophenone groups during the photooxidation of PS was monitored by the changes in absorbance at 240 nm. Fig. 9(a) shows the ratio in

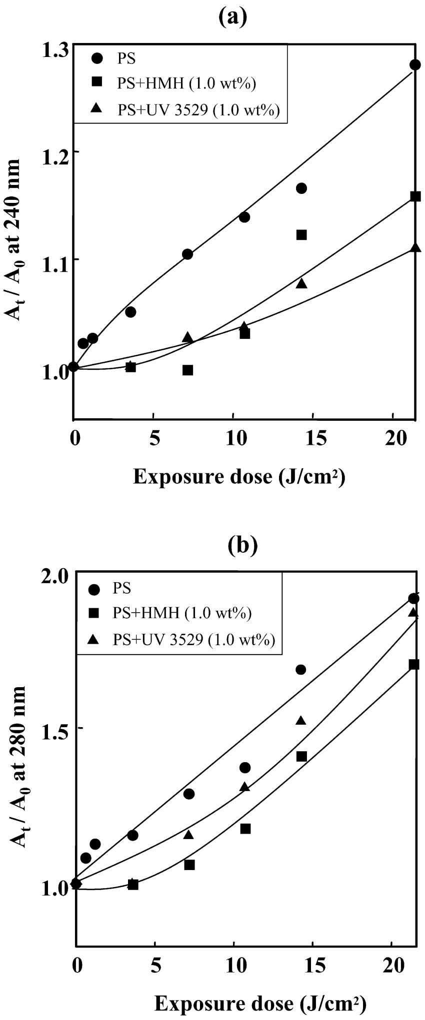


Fig. 10. Plot of A_t/A_0 of the PS films at (a) 240 nm and (b) 280 nm as a function of exposure dose. Irradiations were carried out with 310 nm UV light in air.

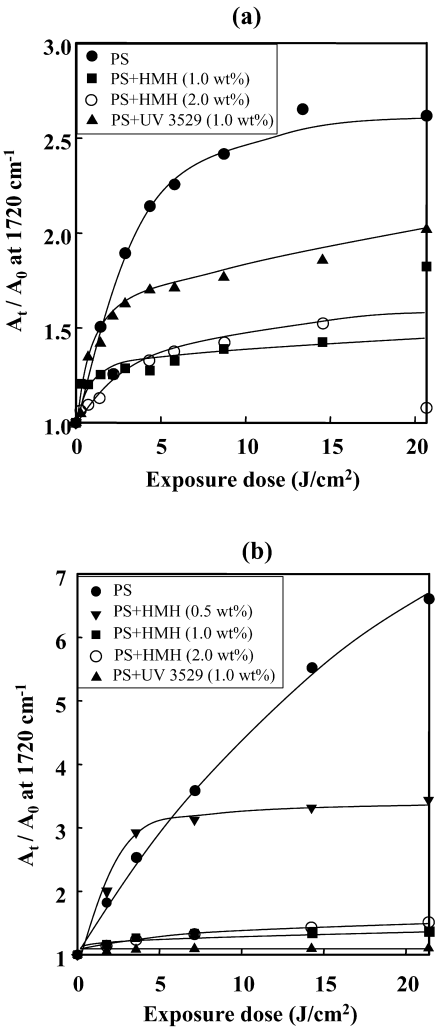


Fig. 11. Plot of A_t/A_0 of the PS films on the KBr pellet at 1720 cm^{-1} as a function of exposure dose. Irradiations were carried out with (a) 254 nm and (b) 310 nm UV light in air.

absorbance (A_t/A_0) of PS films at 240 nm upon irradiation with 254 nm UV light. A_t/A_0 of the PS film containing HMH increased about half of the film without HMH. The photostabilizing efficiency of HMH is similar with that of Cyabsorb UV 3529. This result indicates that HMH effectively decreases the formation of acetophenone groups during the photooxidation of PS.

As a result of the photooxidation of the PS, the absorbance at 280, 310, and 340 nm increased due to the formation of diene, triene, and tetraene groups, respectively [20]. Fig. 9(b) shows A_t/A_0 of the PS films at 280 nm as a function of the exposure dose in the presence or absence of HMH. The formation of diene groups was effectively decreased by the addition of HMH. Similar results were observed at 310 and 340 nm. This result also indicates that HMH effectively decrease the formation of the polyene groups during photooxidation of PS.

The PS film containing HMH was exposed to 310 nm UV light in order to study the effect of HMH on the photooxidation of PS at the different wavelength of irradiation. Fig. 10 shows A_t/A_0 of PS films at (a) 240 nm and (b) 280 nm as a function of irradiation dose upon irradiation with 310 nm UV light. The PS film containing HMH effectively inhibited the formation of acetophenone or polyene groups similar to or better than that containing Cyabsorb UV 3529. However, not so much difference was observed between the cases that irradiations were carried out with 254 or 310 nm UV light except oxidation rate.

The photostabilization of PS by HMH was also monitored by the IR absorption spectral changes. Irradiation of a PS film with 254 nm UV light resulted in the increase of absorbance at 3425, 1724, and 1173 cm^{-1}. An increase in absorbance at 3425 and 1173 cm^{-1} was likely due to the formation of –OOH or –OH groups, while that of 1724 cm^{-1} was due to the formation of C=O groups.

Fig. 11(a) shows A_t/A_0 plot of the PS films on the KBr pellet at 1720 cm^{-1} upon irradiation with 254 nm UV light. The relative photostabilization of PS by the polymeric HALS increased in the order of Cyabsorb UV 3529

(1 wt%) < HMH (1 or 2 wt%). This result shows that HMH has higher photostabilizing efficiency than Cyabsorb UV 3529, when PS was irradiated with 254 nm UV light. Fig. 11(b) shows A_t/A_0 plot of the PS films on the KBr pellet at 1720 cm^{-1} upon irradiation with 310 nm UV light. The relative photostabilization of PS by the polymeric HALS increased in the order of HMH (0.5 wt%) $\ll$ HALS (1 or 2 wt%) $\leq$ Cyabsorb UV 3529. This result indicates that HMH has similar photostabilizing efficiency to Cyabsorb UV 3529, when the PS film containing the polymeric HALS was exposed to 310 nm UV light.

4. Conclusion

Two types of addition polymers, HMH and LMH, were obtained by addition polymerization of DGEBA and ATMP in chlorobenzene. The molecular weight of 1:1 addition polymer of DGEBA and ATMP, HMH and LMH, was 2400 and 600, respectively. The yield of the addition polymer was increased with the amount of ATMP concentration, reaction time, and reaction temperature. The formation of LMH in the addition polymer was favored by low reaction temperature and low ATMP concentration, while that of HMH increased with the reaction temperature and ATMP concentration. The HMH is fairly compatible with PP, PS, and SBR. When irradiations were carried out with 254 or 310 nm UV light, the photostabilization efficiency of HMH in PP was greater than that of Cyabsorb UV 3529, a commercially available polymeric HALS. The photooxidation of PS was decreased with the addition of HMH, and the photostabilization efficiency of HMH in PS was similar to or better than that of Cyabsorb 3529, when irradiations were carried out with 254 or 310 nm UV light. The experimental results indicate that HMH can be utilized as a new polymeric photostabilizer with good compatibility and high photostabilizing efficiency.

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