

## COMMUNICATION

# PHOTOSTABILIZATION OF STYRENE-BUTADIENE RUBBER BY A POLYMERIC HINDERED AMINE LIGHT STABILIZER

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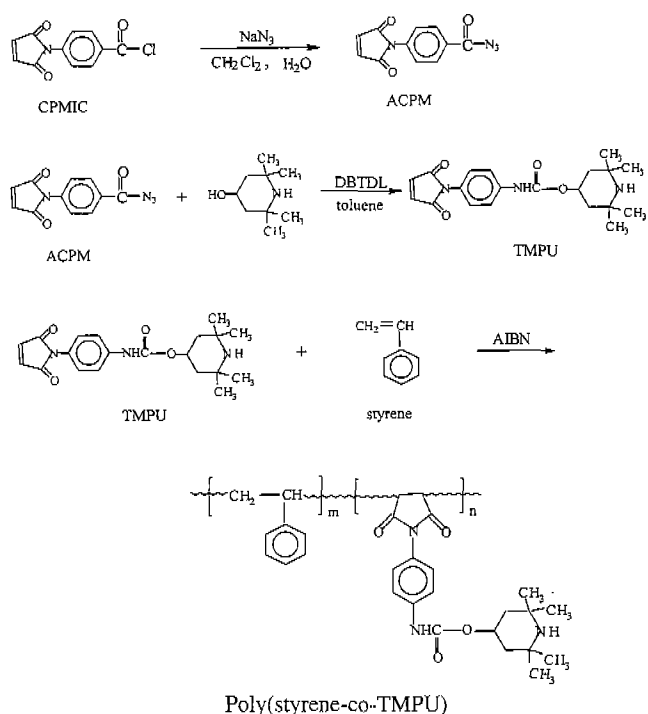
The energy of sunlight around 290 ~ 400 nm photocleaves the chemical bonds of polymer chains to produce free radicals which initiate photodegradation of the polymer molecules resulting in the discoloration, cracking of surface, stiffening, and decrease in the mechanical properties of the polymeric products. For this reason, a light stabilizer should be added to outdoor polymeric products in order to minimize the unwanted effects of sunlight.

UV light stabilizers can be divided into three types depending on the reaction mechanism: i.e., UV absorbers, quenchers, and hindered amine light stabilizers (HALS). Among them, HALS are known to be the most effective photostabilizers for polymers.<sup>1</sup> Free radicals, which are produced by photolysis reaction, can be effectively removed by HALS. This results in inhibiting photooxidation. The compound 2,2,6,6-tetramethylpiperidine, a starting material for the HALS derivatives, was reported for the first time in 1894, and was later commercialized in 1975 by Ciba-Geigy under the trade name Tinuvin 770.

HALS have been used in a large number of commercial polymers, predominantly in styrenic and engineering plastics. They are efficient and cost-effective in many applications, despite their high prices. However, low molecular weight HALS vaporize 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 depositions on the polymer surfaces, a phenomenon known as "blooming". These drawbacks caused by the low molecular HALS can be overcome through the use of the polymeric HALS.

In previous studies at this laboratory, we reported on the preparation of a polymeric photostabilizer containing HALS groups and its photostabilization effects on polystyrene.<sup>2</sup> The present study deals with the preparation and properties of a new polymeric photostabilizer containing HALS groups and its effects on the photooxidation of styrene-butadiene rubber (SBR), the most commonly used rubber in the tire and footwear industry.<sup>3</sup>

The synthetic scheme for the preparation of polymeric HALS is shown in Scheme 1. *N*-[4-(Chlorocarbonyl)phenyl]maleimide (CPMIC) was prepared following the procedure in the literature.<sup>4</sup> *N*-[4-(Azidocarbonyl)phenyl]maleimide (ACPM) was prepared by the reported procedure.<sup>5</sup>



Scheme 1. Synthetic route for the preparation of polymeric HALS.

*N*-[4-(2,2,6,6-tetramethylpiperidin-1-yl)oxy]maleimide (TMPU) was prepared from ACPM (2.0 g, 8.2 mmol) and 2,2,6,6-tetramethyl-4-piperidinol (1.14 g, 7.2 mmol) in the presence of dibutyltin dilaurate (DBTDL, 0.2 mL, 0.5 mmol) in toluene (60 mL). The mixture was refluxed at 110°C for one day. The precipitate was removed by hot filtration and a white solid was formed upon cooling to room temperature. The precipitate was filtered and recrystallized from methanol to give the product in 79% yield.<sup>6</sup>

The polymeric HALS was prepared from copolymerization of TMPU (0.23 g, 0.6 mmol) and styrene (5, 10, 20 fold molar concentration of TMPU) in the presence of AIBN (1 wt%) in THF (2 mL). The mixture was purged with nitrogen for 20 min. Polymerization was carried out at 70°C for 12 hours. The resulting polymer was purified by double precipitation in methanol. Preparation conditions and physical properties of the copolymers are listed in Table 1.

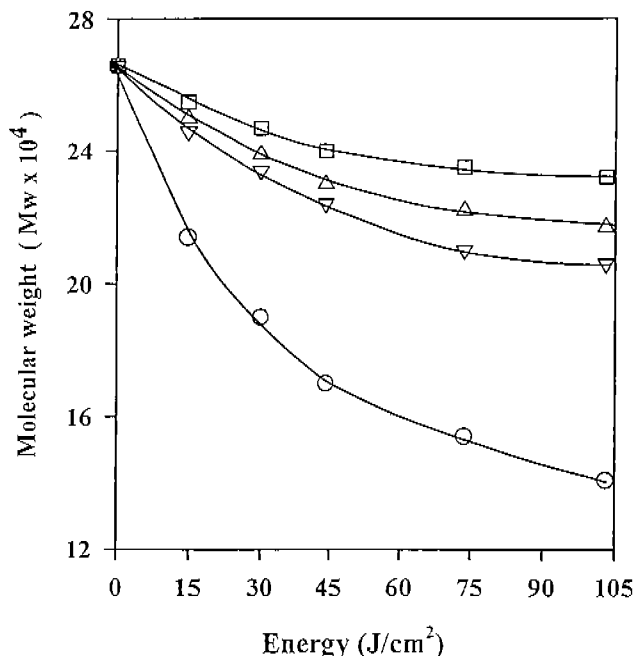


Figure 1. Molecular weight changes of SBR films ( $\circ$ ) containing 10 wt% of copolymer I ( $\square$ ), II ( $\triangle$ ), and III ( $\nabla$ ), as a function of irradiation energy.

The molecular weights of the copolymers increased with increasing the amount of styrene in the feed. As the amount of TMPU increased in the feed, the yield of the copolymer decreased, due to the radical scavenging effect of the HALS groups. The intrinsic viscosity, measured in DMF, ranged from 0.24 to 0.53 g/dL, and the molecular weights were in the range of 5300 ~ 14800.

Molecular weight changes of SBR upon irradiation with 254 nm UV light in the films were observed through GPC (gel permeation chromatography). Fig. 1 shows molecular weight changes of the SBR film containing 10 wt% of the copolymer as a function of irradiation energy. Molecular weights significantly decreased with increasing irradiation energy. The molecular weight of the SBR, without addition of the copolymer, decreased from 266,000 to 141,000 upon irradiation of 103 J/cm<sup>2</sup>. However, a decrease in the molecular weight of the SBR was effectively inhibited by addition of the polymeric HALS. The inhibiting effect of photooxidation of the SBR increased with the number of HALS

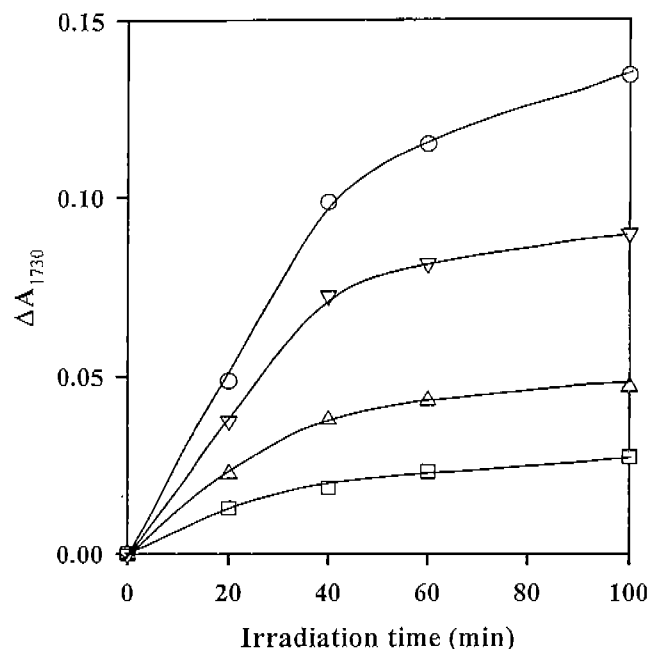


Figure 2. Changes in absorbance of SBR film ( $\circ$ ) containing 10 wt% of copolymer I ( $\square$ ), II ( $\triangle$ ), and III ( $\nabla$ ) at 1730 cm<sup>-1</sup> as a function of irradiation time.

units in the copolymers. Approximately 70% of the photooxidation was inhibited for the SBR containing copolymer I upon irradiation with 103 J/cm<sup>2</sup>.

The effect of polymeric HALS on the photooxidation of SBR was observed through FT-IR absorption spectroscopy. SBR (0.1 g) or SBR with the copolymer (0.1 g, 10 wt%) was dissolved in 8 ml of THF and coated on the KBr pellet. IR spectral changes of the SBR films on the KBr pellet were observed upon irradiation with 254 nm UV light. The absorbance of the SBR film at 1730 cm<sup>-1</sup> increased with irradiation time. This result indicates that photooxidation of SBR took place upon irradiation. The rate of photooxidation of SBR, observed by the changes in absorbance at 1730 cm<sup>-1</sup>, decreased with the addition of the copolymer, as shown in Fig. 2. The relative inhibiting effect of SBR photooxidation increased in the order of the copolymer III < II < I. This result indicates that the copolymer containing a larger amount of TMPU units has a better photostabilization effect on SBR.

Table 1. Results of Polymerization for Copolymers

Copolymer <sup>a</sup>	Monomer feed		Mol% of TMPU in feed	Yield (%)	TMPU unit in the copolymer <sup>b</sup> (mol%)	$\eta_{int}^c$ (g/dl)	$M_w^d$	$M_w/M_n$
	TMPU(g)	Styrene(g)						
I	0.23	0.31	17	43	28	0.24	5,300	1.83
II	0.11	0.31	9	56	18	0.47	10,100	1.63
III	0.11	0.64	5	62	5	0.53	14,800	1.68

<sup>a</sup> Polymerization was carried out in THF at 70°C for 12 hours; AIBN, 1 wt%. <sup>b</sup> Determined from 300 MHz NMR spectra. <sup>c</sup>  $\eta$  was measured in DMF at 25°C. <sup>d</sup> GPC measurement with a column, Styragel HR 3; flow rate, 1 mL/min; solvent, THF.

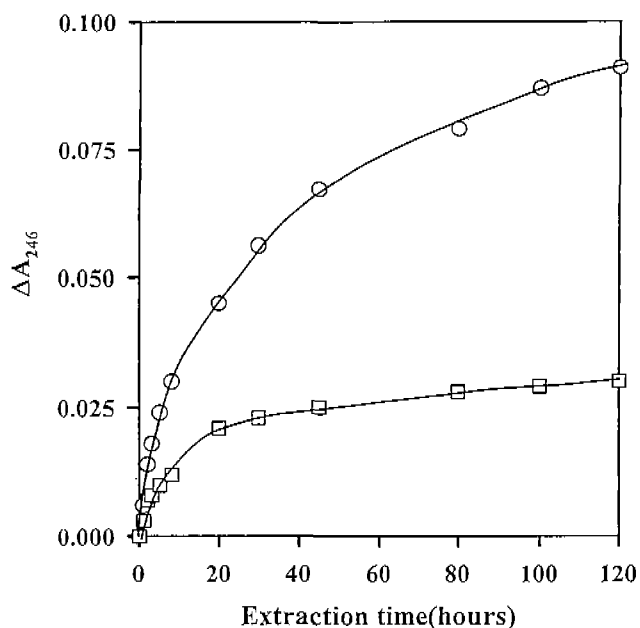


Figure 3. Absorbance changes of the water solution containing SBR with TMPU (○) and SBR with copolymer III (□) blend as a function of extraction time at 90°C.

Low molecular weight HALS have poor extraction resistance. To determine whether the polymeric HALS could overcome this disadvantage of low molecular weight HALS or not, extraction resistance was observed through UV absorption spectroscopy. The SBR film containing TMPU or copolymer III was immersed in water at 90°C, and the absorbance of water solution at 246 nm was measured. The amount of TMPU in the SBR was adjusted to the amount of TMPU units in the copolymer. Fig. 3 shows the UV absorbance changes of water solution as a function of irradiation time. The absorbance of water solution immersed with the SBR containing TMPU continuously increased with extraction time, while that containing copolymer III was stabilized after 20 of extraction time.

In summary, the polymeric HALS prepared by the copolymerization of styrene with TMPU effectively inhibited the

photooxidation and photodegradation of SBR, and exhibited high extraction resistance compared with low molecular weight HALS. A more detailed study on the properties of this polymeric photostabilizer is in progress.

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## REFERENCES

1. Klemchuk, P. P. (1985) *Polymer Stabilization and Degradation*, ACS Symposium Series 280, American Chemical Society, Washington, DC.
2. Chae, K. H., J. -S. Oh and H. S. Ham (1996) Preparation of polymeric photostabilizers containing HALS groups and their photostabilization effects on polystyrene. *J. Photoscience* **3**, 167-169.
3. Brydson, J. A. (1998) *Rubbery Materials and Their Compounds*, Elsevier Applied Science, London and New York, pp. 99-123.
4. Oishi, T. and M. Fujimoto (1992) Synthesis and polymerization of N-[4-N'-( $\alpha$ -methylbenzyl)aminocarbonylphenyl]maleimide. *J. Polym. Sci., Polym. Chem. Ed.* **30**, 1821-1830.
5. Chang, J. Y., T. J. Kim, M. J. Han and K. H. Chae (1999) Polymerization of N-[4-(azidocarbonyl)phenyl]maleimide polymers containing aromatic isocyanate precursors. *Polymer*, **40**, 4049 - 4054.
6. Analytical data for TMPU: mp 203-205 °C; IR (KBr) 3332, 2979, 1714, 1600, 1537, 1398, 1313, 1242, 1058, 839, 686 cm<sup>-1</sup>; UV (CHCl<sub>3</sub>)  $\lambda_{max}$  246.5 nm; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) 7.50, 7.48 (doublet, aromatic, 2H), 7.29, 7.26 (doublet, aromatic, 2H), 6.84 (singlet, imide CH, 2H), 6.69 (singlet, urethane NH, 1H), 5.19 (broad, piperidine NH, 1H), 2.05, 2.01 (doublet, piperidine CH<sub>2</sub> exo or endo, 2H), 1.27, 1.18 (doublet, 4CH<sub>3</sub>, 12H), 1.22-1.0 (broad, piperidine CH and exo or endo CH<sub>2</sub>, 3H).