

## COMMUNICATION

# PREPARATION OF POLYMERIC PHOTOSTABILIZERS CONTAINING HALS GROUPS AND THEIR PHOTOSTABILIZATION EFFECTS ON POLYSTYRENE

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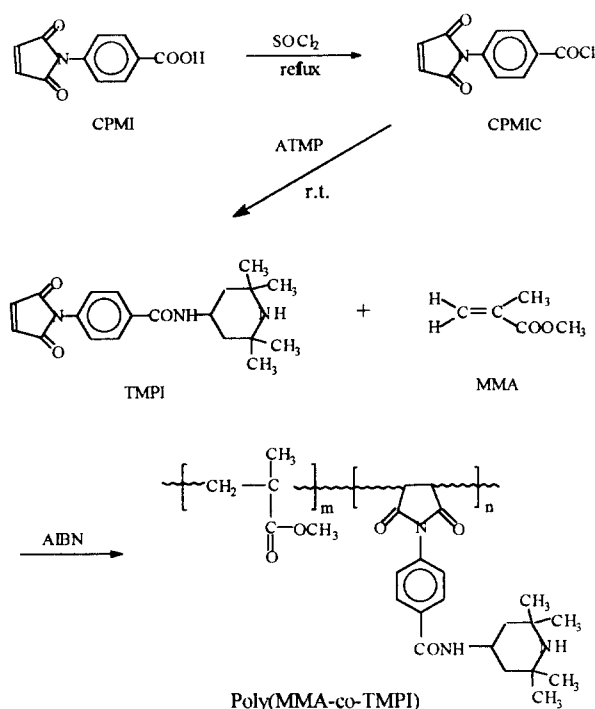
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Absorption of UV light induces photocleavage of polymer chains to produce free radicals which initiate photodegradation of the polymer molecules. Discoloration, cracking of surface, stiffening, and decreasing of mechanical properties of polymeric products occur as a result of photodegradation of the polymers. Photostabilizers are added to the polymer systems in order to minimize the unwanted effects of UV light.

It is well known that Hindered Amine Light Stabilizers (HALS) are one of the most effective photostabilizer for polymers.<sup>1</sup> HALS have been used in a large number of commercial polymers and predominantly used 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 deposition on the polymer surfaces called "blooming". These drawbacks of low molecular HALS can be overcome by use of the polymeric HALS.<sup>2-6</sup> We have been studying photochemical reactions of the polymer systems.<sup>7-11</sup> The present paper reports the preparation of a new polymeric photostabilizer containing HALS groups and their stabilization effects on photooxidation of polystyrene.

The synthetic scheme for the preparation of polymeric photostabilizers containing HALS groups were shown at Scheme 1. N-[(Chloroformyl) phenyl]maleimide (CPMI) and N-[4-(chlorocarbonyl) phenyl]maleimide (CPMIC) were prepared by the known procedure.<sup>12</sup> N-[4-N'-(2,2,6,6-tetramethyl-4-piperidiny)-aminocarbonyl-phenyl] maleimide (TMPI)<sup>13</sup> was prepared by the reaction of CPMI with 4-amino-2,2,6,6-tetramethylpiperidine (ATMP). *p*-CPMIC (1.0 g,



Scheme 1

4 mmol) dissolved in 15 mL of purified chloroform was added dropwise to ATMP (0.63 g, 4 mmol) in 2 mL of chloroform and stirred for 6 h at room temperature. White precipitate was filtered and crystallized from ethanol to give 0.7 g of product (56% yield).

The polymeric HALS was prepared by radical copolymerization of MMA and TMPI in DMF. Solution of TMPI and MMA containing AIBN in 2 mL of DMF was purged with nitrogen for 20 min and heated at 70 °C for 12 h. The polymer was then isolated by precipitation into ethyl acetate and purified by reprecipitation from DMF into acetone. Preparation conditions and physical properties of the copolymers are shown at Table 1.

The copolymers are soluble in DMF, methanol, and DMSO but insoluble in DMAc, THF, and xylene. As the TMPI unit in the copolymer increased, yield of the

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Table 1. Results of Polymerization for Poly(MMA-*co*-TMPI)

Copolymer <sup>a)</sup>	Monomer (g)		Monomer feed (M <sub>1</sub> : M <sub>2</sub> )	AIBN (mol %)	Yield (%)	Copolymer composition (M <sub>1</sub> : M <sub>2</sub> , mol %) <sup>b)</sup>	$\eta_{int}^{c)}$ (g/dL)
	TMPI M <sub>1</sub>	MMA M <sub>2</sub>					
Copolymer 1	0.1	0.3	9 : 91	0.2	61	6 : 94	0.10
Copolymer 2	0.1	0.6	5 : 95	0.4	90	3 : 97	0.15

<sup>a)</sup> Polymerization was carried out in 2 ml of DMF at 70 °C for 6 h.

<sup>b)</sup> Determined from 300 MHz NMR spectra.

<sup>c)</sup>  $\eta$  was measured in DMF for copolymer 1 and MeOH for copolymer 2 at 25 °C : polymer conc., 0.5 g/dL.

copolymer decreased because of radical scavenging effect of TMPI units. Intrinsic viscosity of the copolymer was measured at 25 °C for copolymer 1 to be 0.1 and for copolymer 2 to be 0.15 dL/g, respectively. TGA analysis showed that copolymer 1 begin to decompose at 266°C. DSC analysis showed that T<sub>m</sub> of copolymer 1 was observed at 162 °C.

The IR spectra of the copolymers show that N-H absorption band of TMPI units appears at 3300 cm<sup>-1</sup> and carbonyl absorption band of MMA units appears at 1710 cm<sup>-1</sup>. Other absorption bands are similar to that of PMMA. 300MHz NMR spectra of the copolymers in DMSO-d<sub>6</sub> show that the proton of amide group appears at 8.6 ppm, phenyl group at 7.0-8.0 ppm, and methoxy group of MMA unit at 3.6 ppm. The protons of piperidine ring appear around 1 ppm and main chain protons appear at 1-2 ppm. The mole ratio of MMA units to TMPI units was determined to be 94:6 for copolymer 1 and 97:3 for copolymer 2 by <sup>1</sup>H-NMR

spectroscopy. Somewhat lower incorporation of TMPI in the copolymer may be due to the steric effects of TMPI units.

Polystyrene easily photodegrades upon irradiation with 254 nm UV light. HALS's are known as an effective photostabilizer for the styrenic plastics. The photostabilization effect of polymeric HALS was demonstrated by inhibition effect on the polystyrene photooxidation. Effects of polymeric photostabilizers on the photooxidation of polystyrene were studied by the viscosity measurements in solution state and by the molecular weight measurements by GPC in solid film state.

Polystyrene (0.1g) and copolymer (0.02g) were dissolved in 20 mL of DMF. The solution was filtered through a milipore filter and purged with nitrogen for 20 min. It was irradiated with 254 nm UV light.<sup>14</sup> Relative viscosity was measured as a function of irradiation time at 20 °C. Figure 1 shows that viscosity

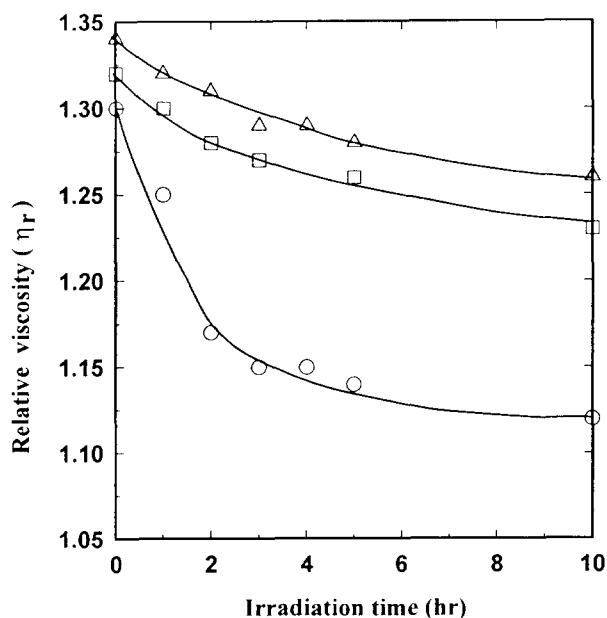


Figure 1. Changes of relative viscosity of polystyrene in DMF solution (0.5 g/dL) as a function of irradiation time: (○), polystyrene; (□), polystyrene with copolymer 1; (△), polystyrene with copolymer 2.

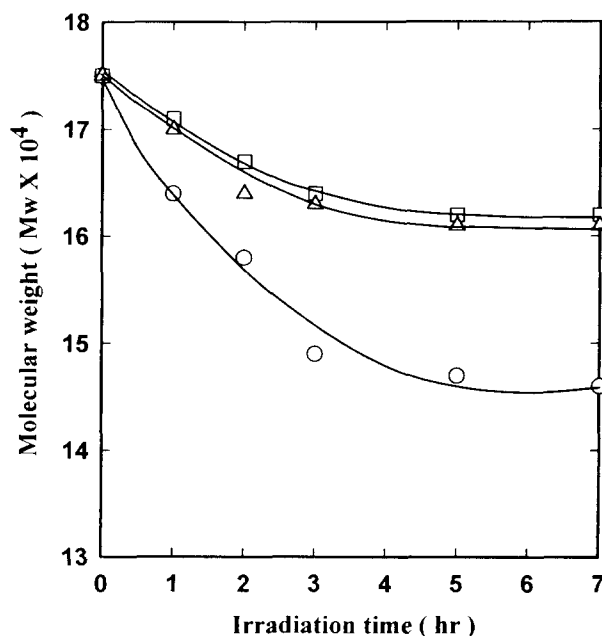


Figure 2. Changes of molecular weight of polystyrene as a function of irradiation time in solid film state: (○), polystyrene; (□), polystyrene with copolymer 1; (△), polystyrene with copolymer 2.

decrease of polystyrene is efficiently inhibited by addition of polymeric HALS. The effect of polymer composition on the photooxidation of polystyrene was not observed at the experimental conditions examined.

Molecular weight changes in the solid film state upon irradiation with 254 nm were observed. Polystyrene (0.2 g) and polymeric HALS (0.02 g) were dissolved in 2 mL DMF. The solution was coated on a glass plate and dried at 150 °C for 30 min.

The polymer film on glass plate was irradiated and molecular weight was measured. Figure 2 shows the molecular weight changes of polystyrene as a function of irradiation time. The decrease of molecular weight of polystyrene is also efficiently inhibited by addition of polymeric HALS. The effect of polymer composition on the photooxidation of polystyrene was not also observed. This is probably due to the efficient radical scavenging effect of HALS groups. The detailed study on the polymeric photostabilizer will be pursued further at this laboratory.

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13. The structure of this compound was identified by IR and <sup>1</sup>H-NMR spectroscopy. mp 226 °C: IR (KBr) 3300, 1765, 1610, 1540, 1480, 1400 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) 8.61 (d, 1H), 7.97 and 7.46 (dd, 4H in phenyl group), 7.22 (s, 2H), 4.37 (s, 1H), 1.96 (d, 2H), 1.66 (t, 2H), 1.47 (d, 12H), 1.05 (t, 1H).
14. Irradiations were carried out in a Rayonet photochemical reactor (The New Southern California Company model RPR-100) equipped with seven 254 nm fluorescent lamps. The power of each lamp was 15 W.