

Synthesis of New Polymeric Stabilizers for Polymers

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ABSTRACT: A monomeric stabilizer (M), 2,2,6,6-tetramethyl-4-piperidinyl(6-methacryloyl amino)hexyl carbamate-1, was synthesized by a two-step controlled isocyanation in which methacrylic acid (MAA) reacted in the first step with hexamethylene diisocyanate (HMDI) at a 1 : 1 mol ratio to form an addition product containing one isocyanate group and one unsaturated double bond. In the second step, this product was reacted with 2,2,6,6-tetramethyl-4-piperidinol (TMP) in a 1 : 1 mol ratio at 80°C in the presence of a catalyst dibutyltin dilaurate (DBTDL) to yield M. A new polymeric stabilizer, copolymer P1, was produced from M with methyl methacrylate (MMA) and another copolymer P2 was produced by reacting M with 2-hydroxy-4-benzophenonyl allyl carbamate (AI-DHBP). Azobisisobutyronitrile (AIBN) was used as an initiator. Their structures, thermal stability, extraction resistance, solubility in organic solvents, and stabilizing effectiveness against photooxidation and thermal oxidation of polypropylene (PP) were characterized by IR, NMR, TGA, and elemental analysis. The results show that both the monomeric and the polymeric stabilizers possess a stabilizing action for protecting PP against photooxidation and thermal oxidation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 403–411, 2000

Key words: high molecular weight stabilizers; synthesis; characterization

INTRODUCTION

Polymer materials exposed to sunlight or used at elevated temperatures or even stored at room temperature in air undergo degradation which shortens their service life; the former is associated with photooxidation, and the latter is mainly a consequence of thermal oxidation. There are several ways to prevent thermal oxidation and photooxidation of polymers: Addition of stabilizers (antioxidants and light stabilizers) is still the most convenient and effective way as this addi-

tion will not alter processing conditions to any significant extent and there are many effective stabilizers from which to choose.^{1–4} It is well known that hindered amine light stabilizers (HALS) are very effective light stabilizers, for which extensive research and reviews have been published.^{1,3,5–10} However, HALS with low molecular weight (MW) are relatively volatile and easily extracted by liquids.^{1,3,7,8} The effectiveness of low MW HALS is limited. A new trend for light stabilizer development is to prepare HALS with higher MW. Copolymerization of functional monomers containing hindered amine is a very important method for preparing HALS with higher MW. Synthesis of several polymeric HALS has been reported,^{1,8–10} many of them based on derivatives of 2,2,6,6-tetramethyl-4-piperidinyl methacrylate.^{11–14} In this article, we report the synthesis and characterization of a new monomeric HALS and two copolymeric HALS, one con-

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taining both hindered amine groups and hydroxybenzophenone groups.

EXPERIMENTAL

Materials

Hexamethylene diisocyanate (HMDI) and methacrylic acid (MAA) were supplied by the Aldrich Chemical Co. 2,2,6,6-Tetramethyl-4-piperidinol (TMP) and azobisisobutyronitrile (AIBN) as an initiator were supplied by TCI (Tokyo Chemical Industry Co., Japan); 2-hydroxy-4-benzophenonyl allyl carbamate (AI-DHBP) was prepared by known methods.¹⁵ Dibutyltin dilaurate (DBTDL), a catalyst, was supplied by the Fluka Co. DBTDL was in form of an 80% solution in benzene.

Synthesis

Monomeric HALS

Synthesis of 2,2,6,6-Tetramethyl-4-piperidinyl(6-Methacryloylamino)Hexyl Carbamate-1 (M). **Step 1.** To a three-neck flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer was added 0.020 mol HMDI at 60°C under stirring; then a mixture of 0.020 mol MAA in 7 mL benzene was added dropwise under stirring. The reaction was monitored using IR to determine the consumption of the carboxyl acid group in MAA at 1700 and 2650 cm^{-1} . After 3 h, the carboxyl acid group (1700, 2650 cm^{-1}) in MAA disappeared. A solution of an intermediate was formed.

Step 2. The above solution containing the intermediate was added to another three-neck flask containing 0.020 mol TMP and 7 mL benzene at 80°C. The contents were well mixed under strong stirring. The controlled isocyanation of TMP with this intermediate began when 0.01 mL of the catalyst DBTDL was added. Reaction was monitored using IR to determine the consumption of —N=C=O in the intermediate at 2255 cm^{-1} . After 5 h, the IR absorption of —N=C=O at 2255 cm^{-1} in the reaction system disappeared. A white precipitate was formed upon addition of pentane. Filtering and washing the precipitate with pentane (4 \times 50 mL) and drying it in a vacuum oven gave a white powder of product **M** with 99.40% yield.

Copolymerization

Copolymerization of M with MMA. To a three-neck flask equipped with a condenser, a nitrogen

inlet, and a magnetic stirrer was added 0.70 g of the monomeric stabilizer **M** and 5 mL of benzene under vigorously stirring; then, 0.063 g of MMA was added at 60°C under stirring. AIBN, 1 wt %, based on the weight of the monomer, was added as an initiator. The polymerization ran for 10 h at 60°C under stirring. After 10 h, another 1 wt % AIBN based on the original total monomer mass was added to ensure complete polymerization of the monomer. The reaction was continued for another 10 h at the same reaction conditions. The content was precipitated with methanol, filtered, and washed with methanol. A light yellow powder product (**P1**) was obtained. This product was dried to a constant weight in a vacuum oven.

Copolymerization of M with AI-DHBP. Copolymerization of **M** with AI-DHBP was carried out under the same experimental conditions as above using 0.70 g of the monomeric stabilizer **M** in 5 mL of benzene and 0.57 g of AI-DHBP at 60°C under stirring. A yellowish powder product (**P2**) was obtained. The purpose of this synthesis was to incorporate an antioxidant functional group, hydroxybenzophenone, into a stabilizer molecule to make it bifunctional.

Analysis

Infrared (IR) spectra were recorded using a Shimadzu FTIR 8001 Fourier transform infrared spectrophotometer. C, H, and N analytical values were obtained using a Perkin–Elmer 2400 CHN elemental analyzer. Proton-nuclear magnetic resonance (¹H-NMR) spectra were recorded at 90 MHz using a JEOL FX-900 FT-NMR spectrometer, DCCl_3 as a solvent, and tetramethylsilane (TMS) as an internal standard. UV spectra were recorded using a Shimadzu UV-1301 PC UV spectrophotometer with ethanol as a solvent. Thermogravimetric analysis (TGA) was performed using a DuPont 9900 thermal analyzer at 20°C/min heating and 75 mL/min nitrogen flow. A Fisher–John melting point apparatus was employed to determine the melting points of the stabilizers. ESR spectra were obtained from an ESR spectrometer, Model-8400, at 22°C; Mn^{2+} was used as an internal standard.

Photooxidation

Preparation of the polypropylene (PP) film sample containing 0.3 wt % of a stabilizer followed a standard procedure reported earlier.^{16–18} Both

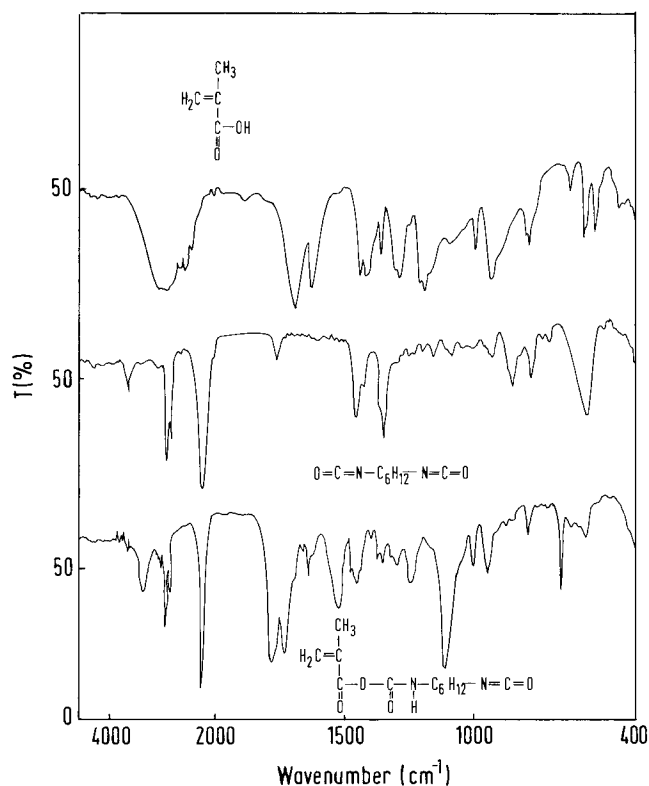


Figure 1 IR spectrum of reaction product of MAA with HMDI.

the test film and the blank film were mounted on the rim of a rotating wheel having a tubular UV lamp mounted at the wheel center. The UV lamp was a 400-W medium-pressure mercury metal halide lamp HPA-400. This lamp does not cause formation of ozone and it emits radiation mainly in the 300–400 nm range and none at 254 nm. The wheel rotated at 4 rpm. The distance between the light source and the samples was 21.5 cm and the test temperature was 30°C in air. A Shimadzu FTIR 8001 Fourier transform infrared spectrophotometer was used to monitor the carbonyl concentration in the test samples at 1710 cm^{-1} . The

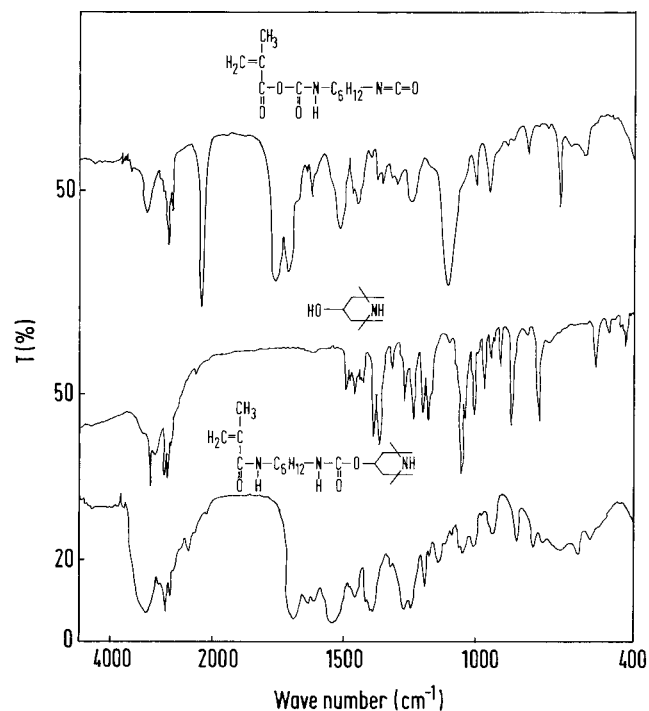


Figure 2 IR spectrum of monomeric stabilizer M produced by controlled isocyanation of HMDI with MAA and TMP.

induction period was determined from a plot of carbonyl absorption versus irradiation exposure time.^{16–18}

Thermal Oxidation

PP film samples containing 0.3% of a stabilizer by weight were prepared using a standard method.^{16–18} Thermal oxidation of the PP film samples and the control sample was carried out in an oven at 140°C in air. A Shimadzu FTIR 8001 infrared spectrophotometer was used to monitor the carbonyl concentration in the test samples at 1710 cm^{-1} . The induction period of the thermal oxidation of the samples was deter-

Table I Characterization of New Monomeric Stabilizer M

| New Peak in Product | IR Change (cm^{-1}) | | NMR (ppm) | | |
|---------------------|--------------------------------|-------|-----------|-----------------|------------------------------|
| | —N=C=O in Reactant | —C=C— | Carbamate | Piperidine Ring | —CH ₂ — from HMDI |
| 1710 | 2255 | 1.94 | 4.90–5.10 | 1.19–1.23 | 1.31–1.40 |
| 3300 | (Disappeared) | 5.25 | | 1.67–1.70 | |
| 1650 | | 5.85 | | 5.00 | |

mined from a plot of carbonyl absorption versus heating time.¹⁶⁻¹⁸

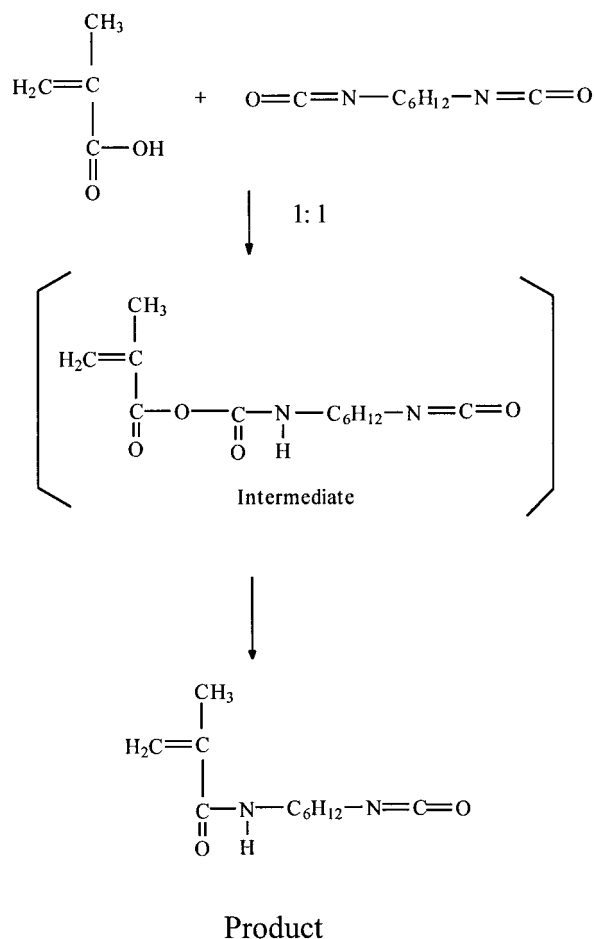
ESR Determination

Oxidized PP film, 0.06 g, was chopped into small pieces and placed in an ESR test tube containing 0.80 mL of toluene. The test tube had a size of 0.50 cm in diameter and 18 cm in length. The PP film was dissolved in the toluene at 110°C in the tube. A gel of PP toluene was formed when the solution was cooled in the tube at 22°C. This PP gel was used for determination of the ESR spectrum. The relative concentration of the nitroxy free radical was determined by a method reported in the literature. Mn^{2+} was used as a comparison standard.

RESULTS AND DISCUSSION

Synthesis of Monomeric Stabilizers

It has been reported in the literature that isocyanate can easily react with alcohol, acid, or phenol in stoichiometric quantities.¹⁹⁻²² Our experimental results show that the reaction between isocyanate and MAA is a stoichiometric, exothermic, direct addition reaction shown in Figure 1, from which it can be seen that an addition product (an intermediate) containing an anhydride (1780 cm^{-1}) and a carbamate group ($1725, 3300\text{ cm}^{-1}$) was formed at the consumption of carboxyl group ($1700, 2650\text{ cm}^{-1}$) in MAA. This intermediate is unstable and it can convert slowly to methacrylic amide containing an isocyanate group below 70°C and rapidly at temperatures higher than 70°C, forming a solid that floats on benzene with the release of carbon dioxide. Adding pentane (50 mL) and washing with pentane ($3 \times 50\text{ mL}$) and filtering showed that no unreacted MAA or isocyanate was found in the filtrate. The product filter cake contains methacrylic amide (1650 cm^{-1}) and $-N=C=O$ (2255 cm^{-1}). Yield was over 90%, indicating that only one of the two $-N=C=O$ groups in HMDI took part in the above addition reaction. Thus, the unreacted $-N=C=O$ in the intermediate can, therefore, be used for further isocyanation with TMP in the second step to produce the monomeric stabilizer M:



Our experimental results also show that the reaction between isocyanate and TMP is a stoichiometric, direct addition reaction. It is a slow reaction without a catalyst at 80°C and a mild reaction in the presence of the catalyst DBTDL.

Structural Analysis

Typical IR spectra of **M** produced from the two-step controlled isocyanation are shown in Figures 1 and 2, from which it can be seen that $-N=C=O$ absorption in the intermediate at 2255 cm^{-1} had disappeared after reacting with TMP at 80°C for 5 h,

Table II Elemental Analysis of Monomeric Stabilizer M

| Calculated (%) | | | Found (%) | | |
|----------------|-------|-------|-----------|-------|-------|
| C | H | N | C | H | N |
| 65.36 | 10.15 | 11.14 | 65.32 | 10.52 | 10.73 |

and a new carbamate group (absorption at 1710 and 3300 cm^{-1}) was formed. The anhydride in the intermediate converted to MAA (1666 cm^{-1}) with the release of carbon dioxide.

Based on information from Figures 1 and 2, one can conclude that the following reactions have occurred:

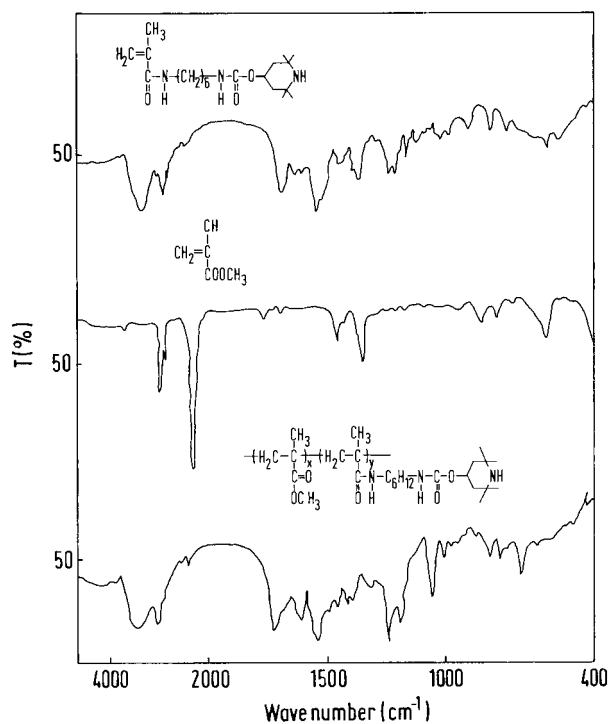
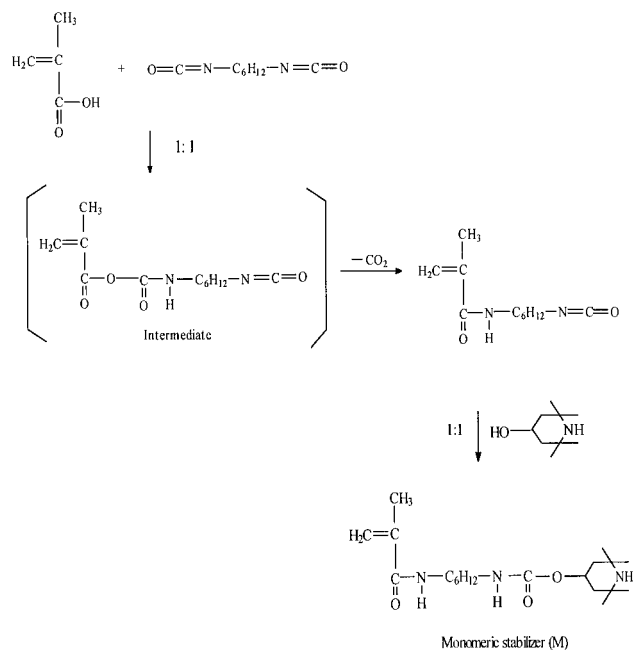


Figure 3 IR spectrum of polymeric stabilizer P1 prepared from copolymerization of M with MMA.

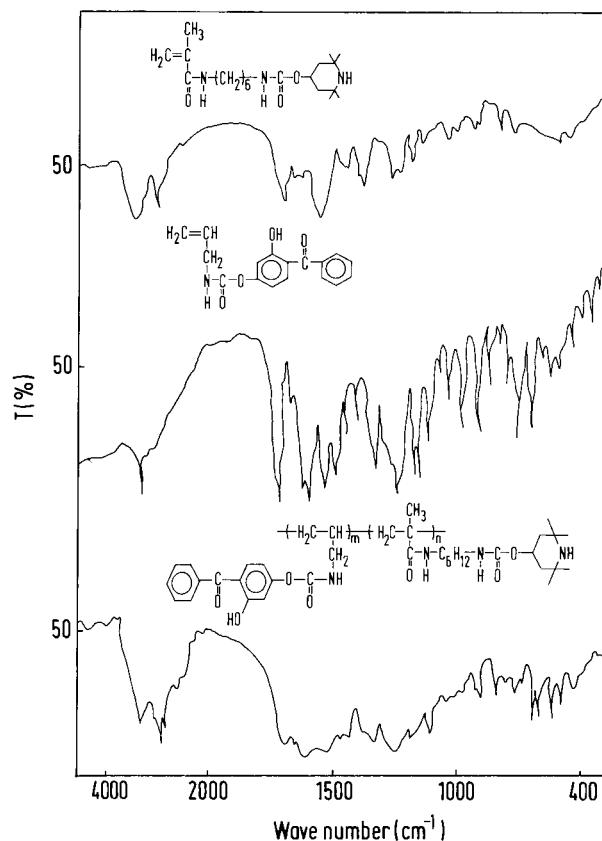


Figure 4 IR spectrum of polymeric stabilizer P2 prepared from copolymerization of M with AI-DHBP.

NMR spectra and elemental analysis of M are shown in Tables I and II. From the corresponding NMR spectrum of M, it can be seen that M contains a double bond (CH_3- , 1.94 ppm; two protons, 5.25 and 5.85 ppm), a carbamate group ($-\text{NH}-$, 4.90–5.10 ppm), and hindered amine ($\text{N}-\text{H}$, 5.00 ppm; 2,2,6,6-tetramethyl, 1.20 and 1.30 ppm; 3,5-two methylenes, 1.60–1.70 ppm). These NMR data further support the conclusions drawn from the IR results. From Table II, it can be seen that the C, H, N contents of M agree very well with results calculated from the structural formula, which render further support to the conclusions drawn from IR and NMR.

Polymeric Stabilizers

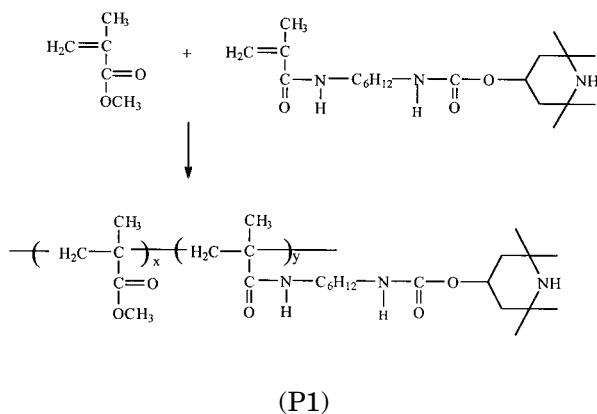
Typical IR spectra of products P1 and P2 are shown in Figures 3 and 4. From Figure 3, it can be seen that after copolymerization of M with MMA the double bonds in the monomers (1640 cm^{-1}) disappeared, indicating that M and MMA were converted to form copolymer P1, a polymeric stabilizer containing γ hindered amine groups:

Table III Solubility of Products M, P1, and P2

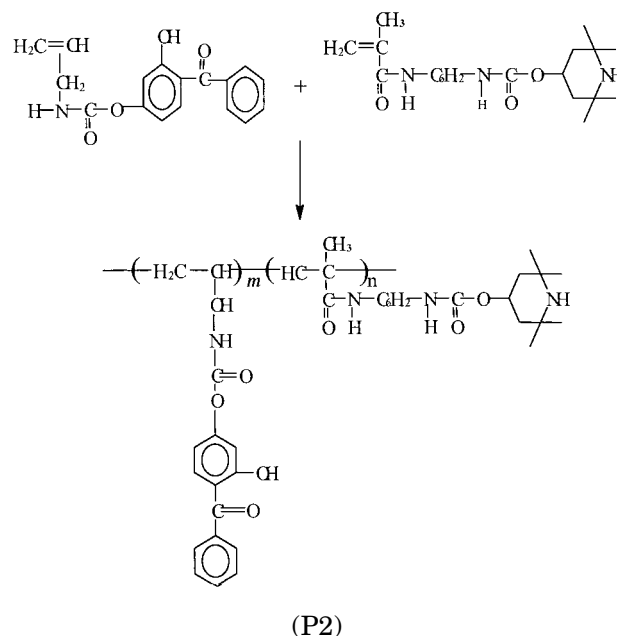
| Solvent | δ^a | M | P1 | P2 |
|---------------|------------|----|----|----|
| Pantane | 7.0 | x | x | x |
| Hexane | 7.4 | x | x | x |
| Cyclohexane | 8.2 | x | x | x |
| Toluene | 8.9 | x | x | x |
| Ethyl acetate | 9.1 | x | x | x |
| THF | 9.1 | hs | hs | hs |
| Benzene | 9.2 | es | hs | hs |
| Chloroform | 9.3 | es | hs | hs |
| Acetone | 9.9 | x | x | x |
| Propanol | 11.9 | s | x | x |
| Ethanol | 12.7 | s | x | x |
| Methanol | 14.5 | s | x | x |
| Water | 23.7 | x | x | x |

s, soluble; es, dissolve easily; hs, hard to dissolve; x, cannot dissolve.

^a δ is the solubility parameter of organic solvents in (cal/mL³)^{1/2}.



From Figure 4, it can be seen that in the copolymerization of M with AI-DHBP the double bonds in M (1640 cm⁻¹) had disappeared, indicating that M and AI-DHBP were converted into copolymer P2, a bifunctional polymeric stabilizer containing *n* hindered amine groups and *m* hydroxybenzophenone groups:



The UV spectrum of P2 contains the similar UV spectrum of the monomer AI-DHBP which has two UV absorptions at 290 and 330 nm, in association with the benzophenone structure unit in AI-DHBP.¹⁵ This result indicates that copolymer P2 had inherited the structural unit of the monomer AI-DHBP through the copolymerization, in agreement with the conclusion drawn from results of IR and NMR. Monomer M and copolymer P1 do not have these UV absorptions as they do not have the benzophenone structure in them.

Properties

The solubilities of products M, P1, and P2 are shown in Table III. From Table III, it can be seen that the copolymers are harder to dissolve in common organic solvents.

Thermal stability test results of these stabilizers are shown in Table IV. From this table, it can be seen that monomeric and polymeric stabilizers are stable in the range 200–260°C.

Table IV Thermal Stability of M, P1, and P2

| Sample | Structural Composition | Appearance | At 20 wt % Loss (°C) | MP (°C) |
|--------|-----------------------------------|---------------------|----------------------|---------|
| M | MAA-HMDI-TMP | White powder | 240 | 91–94 |
| P1 | Copolymer of M with MMA | Light yellow powder | 250 | 250–280 |
| P2 | Copolymer of M with AI-DHBP | Yellow powder | 260 | 245–275 |
| TMP | 2,2,6,6-Tetramethyl-4-piperidinol | White crystalline | 120 | 129–131 |

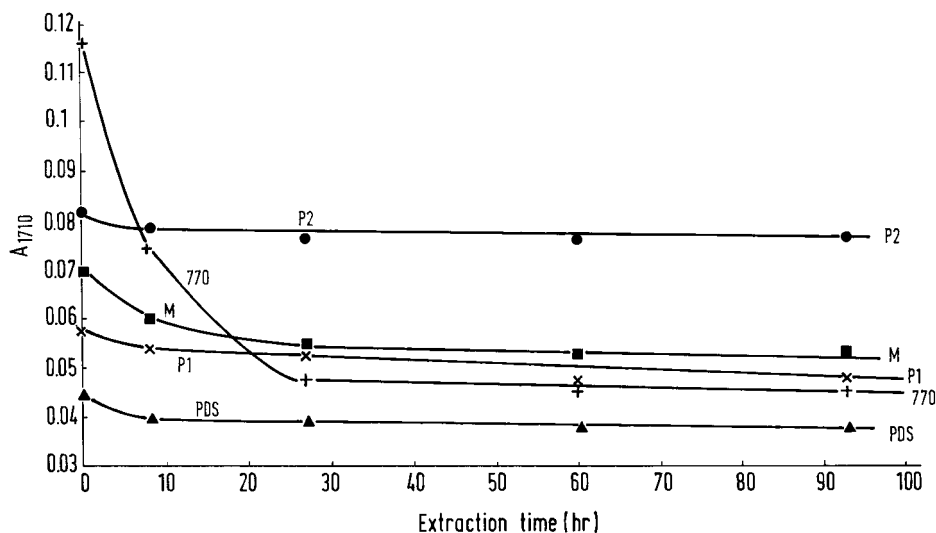


Figure 5 Extraction resistance of stabilizers to water at 90°C.

The resistance of the stabilizers to liquid extraction is shown in Figure 5. As can be expected, the polymeric stabilizers are, in general, more resistant to liquid extraction by water at 90°C than with the lower MW stabilizer.

Stabilizing Ability

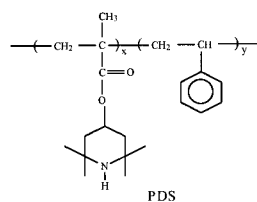
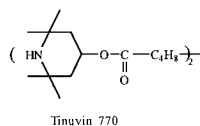
The induction periods of photooxidation and thermal oxidation for PP film containing the stabilizers are shown in Table V. It is very interesting to observe that the presence of the hindered amine group in M, in P1, and in Tinuvin-770 accounts

for the higher effectiveness for protecting PP against thermal oxidation, in the order of 770 > M > P1/P2 > PDS. The photostabilizing action of HALS is associated with the scavenging action of stable nitroxyl free radicals on alkyl free radicals formed from oxidation of the substrate polymers.^{1,3,8} The presence of stable nitroxyl free radicals in our PP film test samples was confirmed by ESR spectra taken of our PP samples containing HALS (Fig. 6).

Figure 6 shows the ESR signal of our HALS-containing PP film after oxidation for 48 h at

Table V Induction Period (IP) of Photooxidation and Thermal Oxidation of PP Film Containing a Stabilizer

| PP Film Containing | IP (Photooxidation) (h) | IP (Thermal Oxidation) (h) | Stabilizer Concentration (%) | MW of Stabilizer |
|--------------------|-------------------------|----------------------------|------------------------------|------------------|
| Blank | 19 | 2 | 0.00 | |
| M | 70 | 92 | 0.30 | 368 |
| P1 | 33 | 71 | 0.30 | 1500–1600 |
| P2 | 32 | 30 | 0.30 | 1600–1700 |
| PDS | 24 | 57 | 0.30 | 3000 |
| Tinuvin-770 | 160 | 117 | 0.30 | 480 |



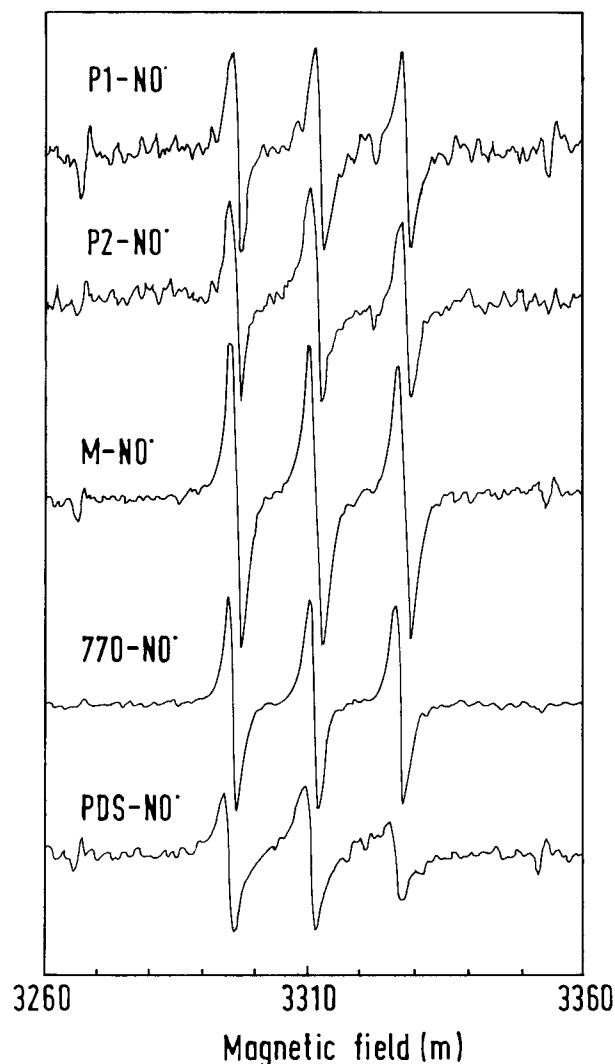


Figure 6 ESR spectra of stable nitroxy free radicals formed in oxidized PP films containing HALS at 140°C for 48 h in air. *ESR signal was obtained in a gel of PP-toluene. X—NO• is a stable nitroxy free radical formed from precursor X, and X is M, P1, P2, Tinuvin-770, and PDS.

140°C in air. They are standard signals of the nitroxy stable free radical with a triplex.^{1,3,8,23–25} Nitroxy free radicals protect substrate polymers against photooxidation; likewise, the stabilizing action of a HALS against the thermal oxidation of polymers is also associated with the scavenging action of nitroxy stable free radicals on alkyl free radicals formed from thermal oxidation of substrate polymers.^{1,3,5–10,23–25}

Further study showed that the relative concentrations of stable nitroxy free radicals in the oxidized PP sample is 770 > M > P1 ≫ PDS > P2 in the proportions of 11.87 : 3.52 : 2.24 : 1.54 : 1,

which is in fair agreement with experimental results shown in Table V.

Induction period (IP) values were estimated from plots of carbonyl concentration measured at 1710 cm⁻¹ versus exposure time. Uncertainties in IP could be as high as ±15%. We added 0.3 wt % (based on mass of substrate) of a stabilizer in a test PP sample. Thus, for P1, P2, and PDS, their hindered amine concentration in a test sample was less than that of 770 due to differences in molecular structure and molecular weights which also affect the diffusion rate of a stabilizer molecule in a substrate. We place higher certainties in the concentration *C* of nitroxy free radicals in the test samples measured using ESR. A fairly linear relationship appears to exist between IP and *C*, from which it can be seen that the higher IP of 770 can be attributed to its higher *C* value.

When two or more than two different stabilizers are used in a substrate, both synergistic and antagonistic effects have been observed.²⁶ More work will be conducted to clarify whether the presence of both hydroxybenzophenone groups and hindered amine groups in P2 is antagonistic or synergistic.

CONCLUSIONS

1. The monomeric stabilizer M, 2,2,6,6-tetramethyl-4-piperidiny (6-methacryloylamino)hexyl carbamate-1, was synthesized by a two-step controlled isocyanation of HMDI with methacrylic acid and TMP.
2. Two polymeric stabilizers P1 and P2 were prepared by free-radical copolymerization of above monomeric stabilizer M with MMA and AI-DHBP, respectively.
3. The monomeric stabilizer M and polymeric stabilizers P1 and P2 can protect PP against photooxidation and thermal oxidation.

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