

# Effect of Penta- and Tetramethyl HALS on the Radiation Resistance of Polypropylene

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**ABSTRACT:** 2,2,6,6-Tetramethyl-4-piperidinyl methacrylate (TMPM), a new penta-methyl HALS 1,2,2,6,6-pentamethyl-4-piperidinyl methacrylate (PMPM), their homopolymers (PTMPM and PPMPM), and their copolymers, [i.e., TMPM or PMPM copolymerized with monomers methyl methacrylate (MMA), methacrylic acid (MAA), acrylic acid (AA), and styrene (St) separately] were synthesized. PMPM shows an extremely excellent stabilizing effectiveness on improving the radiation resistance of polypropylene (PP) in comparison with other low molecular weight (LMW) HALS or polymeric HALS. Polymeric HALS shows a much higher thermal stability and better extraction resistance than that of LMW HALS. It is found that the *E<sub>b</sub>* values of the PP-added pentamethyl HALS series are higher than those of PP with the corresponding tetramethyl HALS series at a given irradiation dose. A conclusion can be drawn that the pentamethyl HALS series has a higher stabilizing effectiveness than that of the tetramethyl HALS series. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2649–2656, 1998

**Key words:** hindered amine light stabilizers (HALS);  $\gamma$ -irradiation; polypropylene; radiation resistance

## INTRODUCTION

Hindered amine light stabilizers (HALS) are the most effective existing light stabilizers protecting polyolefins and other polymers from light-induced degradation; they can also prevent the degradation of polymers from high-energy irradiation. Some research work and reviews have been published.<sup>1–5</sup> Low molecular weight (LMW) HALS are volatile and unstable in the thermal processing<sup>6,7</sup> of polymers, which leads to their very low stabilizing effectiveness. A trend for developing HALS is to prepare polymeric HALS with a higher molecular weight.<sup>1–5</sup> Polymeric HALS are much more stable at high temperature than are LMW HALS. The compatibility of polymeric HALS with polymers is also improved. Copoly-

merization or homopolymerization of functional hindered amine monomers is the usual method for the preparation of polymeric HALS. The usually used hindered amine monomers are based on the chemical structures as 2,2,6,6-tetramethylpiperidines and 1,2,2,6,6-pentamethylpiperidines. It was found that the pentamethyl piperidines were more effective in decomposing hydroperoxide<sup>8,9</sup> and quenching singlet oxygen<sup>10</sup> produced in polymers than are the tetramethyl piperidines, so the development of pentamethyl HALS is one of the trends that have been paid attention to in developing HALS. A search for the most effective HALS on improving the radiation resistance of polyolefins is introduced in this article.

## EXPERIMENTAL

### Materials

2,2,6,6-Tetramethylpiperidinol (TMP) was supplied by Beijing Additives Research Institute

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(Beijing, China). TMPM was synthesized by the authors according to the literature<sup>11</sup>; it was twice recrystallized from hexane before use. Powdered polypropylene (PP) without any additives was supplied by the Yanshan Petrochemical Corp. (Beijing, China; type: 1600, melt-flow index 8.2 g/10 min, and type: 2400, melt-flow index 1.8 g/10 min). Tinuvin 770, Tinuvin 622, and Chimassorb 944 were produced by Ciba-Geigy (Basel, Switzerland). GW-540 was supplied by Taiyuan Chemical Technology Research Institute (Taiyuan, China). (See Appendix.)

### Preparation of HALS

#### *Synthesis of 1,2,2,6,6-Pentamethyl-4-piperidinyl Methacrylate (PMPM)*

PMPM was prepared by a methylation reaction between TMPM and formaldehyde. The boiling point of the liquid product is 154–156°C/3–4 mmHg.

#### *Polymerization*

*Homopolymers.* Poly(2,2,6,6-tetramethyl-4-piperidinyl methacrylate) (PTMPM) and poly(1,2,2,6,6-pentamethyl-4-piperidinyl methacrylate) (PPMPM) were prepared by radical polymerization. AIBN, 1%, based on the monomer was used as an initiator and alcohol was used as a solvent; the reactions were carried out at 80°C for 12 h.

*Copolymers.* The copolymers of TMPM or PMPM with methyl methacrylate (MMA), methacrylic acid (MAA), acrylic acid (AA), and styrene (St) were obtained by radical polymerization. AIBN, 1%, based on the monomer was used as an initiator and alcohol was used as a solvent; the reactions were carried out under 80°C for 12 h.

The homopolymers and copolymers were purified by precipitation with water from an alcohol solution. The white powder was obtained separately.

#### **Characterization of PMPM**

The characterization of the newly synthesized pentamethyl HALS PMPM was carried out. The IR spectrum of PMPM was obtained by a Nicolet 170SX Fourier transform infrared spectrometer (USA). UV analysis was carried out with a DMS-300 UV-visible spectrometer (Varian, Australia); NMR, with a Varian-200 MHz NMR spectrometer

(Australia); and MS, with a Finnigan MAT 4510. Elemental analysis was carried out with a Perkin-Elmer 240-C (USA). Some of these analyses of TMPM were also obtained to compare with those of PMPM.

#### **Thermogravimetry Analyses**

The samples were vacuum-dried before the thermogravimetry analyses. The thermogravimetry analyses of these monomers, polymers, and some LMW HALS were carried out in a TG50 of a TA 3000 thermoanalysis system made by Mettler (Switzerland). The purge gas was N<sub>2</sub>, the flow rate was 15 mL/min, and the heating rate was 20°C/min. The relative thermal stability of these samples was evaluated by comparison of the material loss temperatures  $T_{10}$ ,  $T_{50}$ ,  $T_{90}$ , and  $T_{100}$ , at which samples undergo 10, 50, 90, and 100% decomposition or volatilization.

#### **Extraction Resistance Test of HALS**

HALS, 1% [TMP, PMP, TMPM, PMPM, PTMPM, PPMPM, P(TMPM + St), and P(PMPM + St)] based on the weight of the powdered PP were dissolved in alcohol separately. The solution was then mixed thoroughly with powdered PP. The solvent was removed under reduced pressure and the PP powder was pressed into 100- $\mu$ m-thick film at 190°C. PP films containing HALS were Soxhlet-extracted by alcohol at different times. The weight of the PP film was measured before and after extraction by an M3 microbalance with a precision of 10<sup>-6</sup> g (Mettler).

The PP films containing TMPM or PMPM were irradiated 25 kGy by gamma rays also, then Soxhlet-extracted and measured. The weight loss of the HALS in the PP film was calculated by the equation as follows:

$$\text{Weight loss (\%)} = \frac{W_0 - W_t}{W_0} \times 10,000$$

where  $W_0$  is the weight of the PP film before extraction, and  $W_t$ , the weight of the PP film after extraction at different times (h).

#### **Preparation of Test Samples**

HALS and other additives were mixed with powdered PP and extruded at 200°C, then heated at 190°C for 6 min and molded under a pressure of  $1.47 \times 10^7$  Pa for 4 min and quenched immediately in tap water. The samples were punched

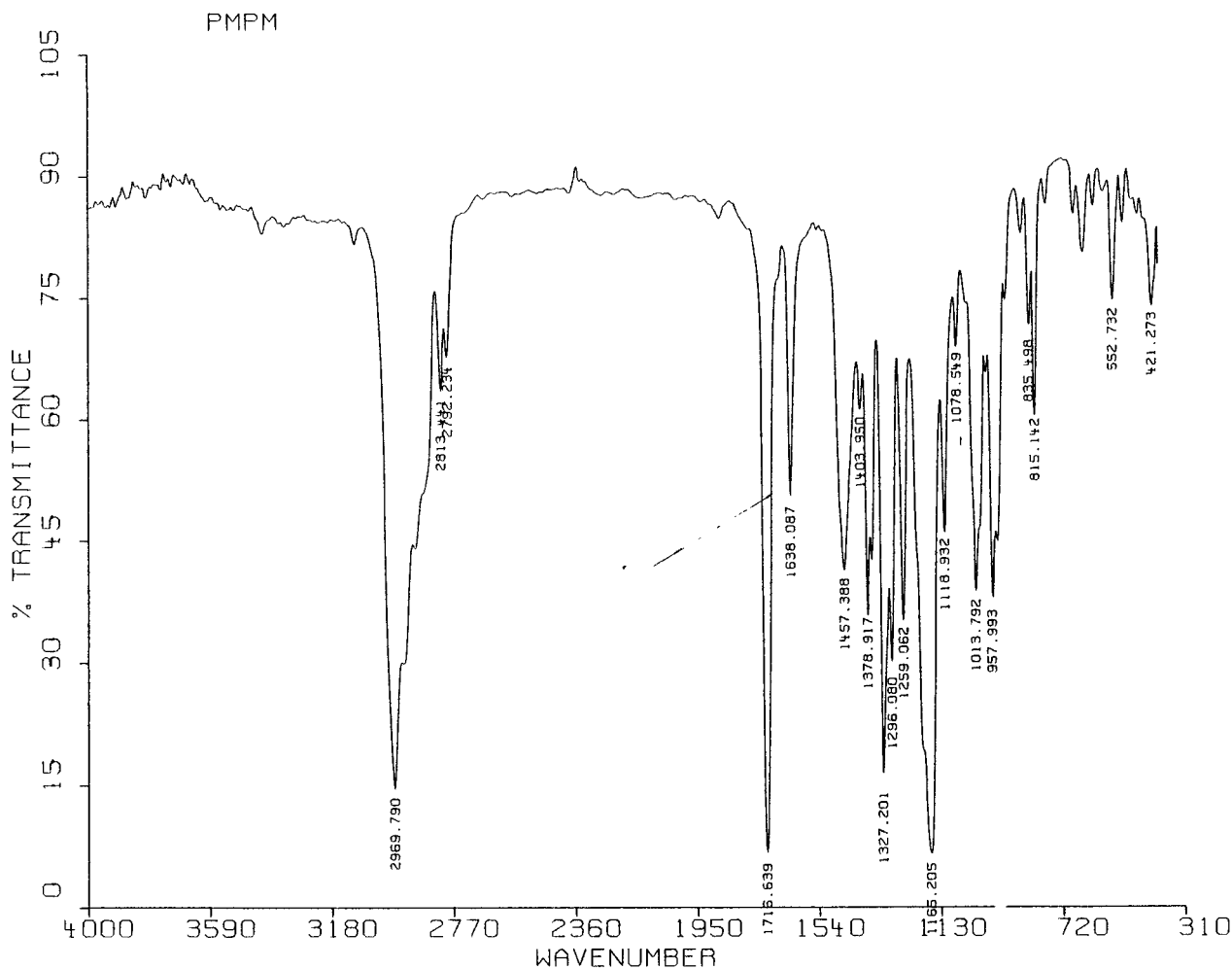


Figure 1 FTIR spectrum of PMPM.

into a dumbbell shape with a neck of 1 mm (thickness)  $\times$  3 mm (width).

#### Irradiation

PP samples were irradiated in a  $^{60}\text{Co}$  gamma chamber. The dose rate was determined by a Fricke dosimeter. All the PP samples were irradiated with different doses at a dose rate of 12 kGy/h in air at room temperature.

#### Test of Elongation at Break

The radiation resistance of the tested samples after irradiation were evaluated by the elongation at break ( $E_b$ ) value. The higher the  $E_b$  value of the PP sample at a given dose shows that it has a higher radiation resistance than that of the other samples. The stress-strain measurements of the dumbbell samples, before and after different dose

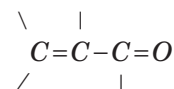
irradiations, were carried out at a crosshead speed of 50 mm/min. The average  $E_b$  value of five samples was taken as the resultant value.

## RESULTS AND DISCUSSION

#### Characterization of PMPM

ANAL: Calcd for  $\text{C}_{14}\text{H}_{25}\text{O}_2\text{N}$ : C, 70.25%; H, 10.53%; N, 5.85%. Found: C, 70.04%; H, 10.91%; N, 5.49%.

The UV spectra show that the  $\lambda_{\text{max}}$  (241.0 nm) of PMPM is very close to the  $\lambda_{\text{max}}$  (240.3 nm) of TMPM as they have the same conjugated double bonds



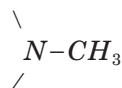
**Table I**  $T_{10}$ ,  $T_{50}$ ,  $T_{90}$ , and  $T_{100}$  of HALS

Sample	$T_{10}$	$T_{50}$	$T_{90}$	$T_{100}$
TMP	123	146	166	178
PMP	110	156	176	181
TMPM	124	179	201	207
PTMPM	297	326	418	485
PPMPM	274	303	385	476
P(TMPM + MMA)	296	349	424	472
P(PMPM + MMA)	269	313	418	474
P(TMPM + MAA)	120	340	434	492
P(PMPM + MAA)	178	350	440	485
P(TMPM + AA)	208	317	428	505
P(PMPM + AA)	210	314	418	487
P(TMPM + St)	312	390	430	462
P(PMPM + St)	280	309	428	461

which induced a  $\pi-\pi^*$  transition. The IR spectrum (Fig. 1) shows that the peak at  $3312\text{ cm}^{-1}$  which contributes to the



bond of TMPM disappears in the spectrum of PMPM and two peaks at  $2814$  and  $2791\text{ cm}^{-1}$  which contribute to the



bond of PMPM appear. The peaks at  $1716$  and  $1638\text{ cm}^{-1}$  that contribute to the



and



bonds, respectively, also appear.

$^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ; ppm): 1.07 (6H, s), 1.15 (6H, s), 1.52 (2H, t), 2.04 (2H, m), 2.10 (3H, s), 2.24 (3H, s), 5.12 (1H, m), 5.53 (1H, s), 6.08 (1H, s). MS: (EI),  $m/z$

(%): 240(M + 1, 11.24), 238(M - 1, 7.77), 154(15.28), 138(55.33), 72(100), 69(33.75).

These analysis results show that the product synthesized is 1,2,2,6,6-pentamethyl-4-piperidinyl methacrylate (PMPM).

### Thermostabilities of HALS

The  $T_{10}$ ,  $T_{50}$ ,  $T_{90}$ , and  $T_{100}$  of LMW HALS 2,2,6,6-tetramethylpiperidinol (TMP), 1,2,2,6,6-pentamethylpiperidinol (PMP), TMPM, and the homopolymers of TMPM and PMPM and their copolymers are shown in Table I.

It can be seen that the  $T_{10}$ ,  $T_{50}$ ,  $T_{90}$ , and  $T_{100}$  of LMW HALS (TMP, PMP, and TMPM) are lower or just a little higher than  $200^\circ\text{C}$ . This result shows that the LMW HALS are unstable under heating. Most of them will volatilize or thermally decompose under the thermal processing temperature of polyolefins,  $200^\circ\text{C}$  for PP, when they are added into polyolefins as stabilizers. However, when the monomeric HALS TMPM and PMPM are polymerized, these polymeric HALS (PTMPM, PPMPM, and the copolymers) cannot volatilize even under the highest heating temperature in the TG analyses. The material loss of them in TGA should be due almost to thermal decomposition. The  $T_{10}$ ,  $T_{50}$ ,  $T_{90}$ , and  $T_{100}$  of polymeric HALS are higher than  $200^\circ\text{C}$  excluding the  $T_{10}$ s of P(TMPM + MAA) and P(PMPM + MAA), which are lower than  $200^\circ\text{C}$ . These polymeric HALS do not decompose in the thermal processing of polyolefins. These analyses show that polymeric HALS have a much higher thermal stability than that of LMW HALS.

### Extraction Resistance Test of HALS

The results of the solvent extraction resistance test of LMW HALS and polymeric HALS is shown

**Table II** Weight Loss of HALS in PP Film Extracted by Alcohol at Different Times

HALS	2 h (%)	6 h (%)	16 h (%)
TMP	74	81	89
PMP	60	82	89
TMPM	70	75	88
PMPM	58	75	94
PTMPM	0	21	23
PPMPM	0	13	22
PDS	0	0	20
PPS	0	0	14

**Table III Weight Loss of TMPM and PMPM in PP Film Irradiated 25 kGy Extracted by Alcohol at Different Times**

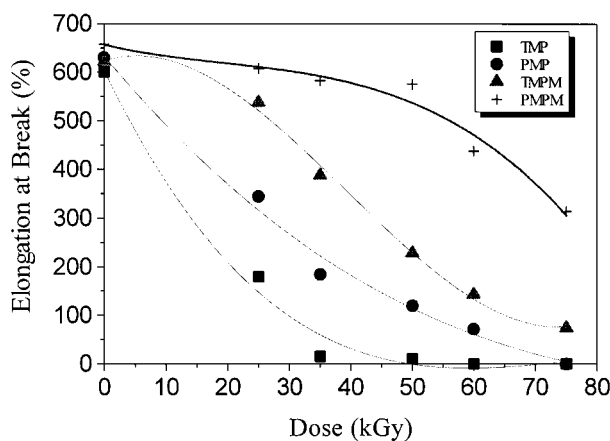
HALS	2 h (%)	6 h (%)	16 (%)
TMPM (1%, unirradiated)	70	75	88
TMPM (1%, irradiated)	54	66	79
PMPM (1%, unirradiated)	58	75	94
PMPM (1%, irradiated)	52	64	76

in Table II. LMW HALS (TMP, PMP, TMPM, PMPM) can be very easily extracted from PP film by a solvent. Their weight loss is above 50% after 2-h extraction and about 90% after 16-h extraction. These results show that LMW HALS have a very bad solvent extraction resistance. On the contrary, polymeric HALS [PTMPM, PPMPM, P(TMPM + St), P(PMPM + St)] show much a better extraction resistance. The weight loss of polymeric HALS is zero after 2-h extraction and only about 20% after 16-h extraction.

Table III shows that the weight loss of TMPM or PMPM in PP films irradiated are lower than those in PP films unirradiated. These results indicate that some of these two LMW HALS with polymerizable double bonds may polymerize or graft onto PP when they are irradiated by gamma rays. The monomeric HALS change to polymeric HALS, so they cannot so easily be extracted by solvent as LMW HALS.

#### Radiation Resistance of PP with Various HALS

Figure 2 shows that the  $E_b$  value of the PP samples added to various LMW HALS TMP, PMP, TMPM, and PMPM separately (all the following



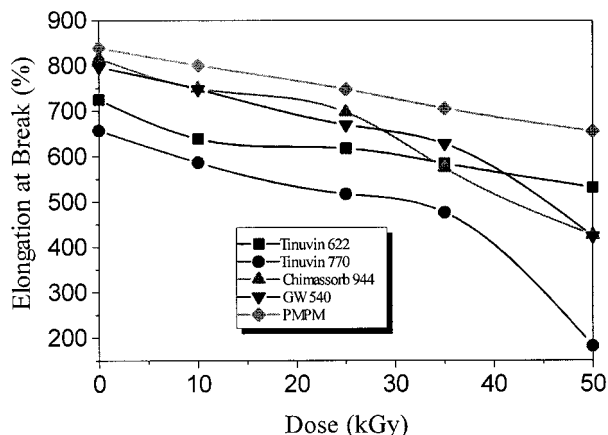
**Figure 2**  $E_b$  values of PP-TMP, PP-PMP, PP-TMPM, and PP-PMPM versus dose.

PP samples are represented by the symbols of PP-HALS added, such as PP-TMP, PP-PMP, PP-TMPM, and PP-PMPM) versus different doses. According to the  $E_b$  values versus dose, the order of radiation resistance of these PP samples is PP-PMPM > PP-TMPM > PP-PMP > PP-TMP, that is, the radiation resistance of the PP-TMP sample is the lowest one of the four; its  $E_b$  value drops to zero at 35 kGy. The PP-PMP sample has a higher radiation resistance than that of PP-TMP; its  $E_b$  value reduces to one-half of the sample unirradiated and is 156% after 50 kGy irradiation. The PP-TMPM and PP-PMPM samples have a higher radiation resistance than that of the PP-TMP and PP-PMP samples. The PP-PMPM sample shows the highest radiation resistance; its  $E_b$  value decreases very little at 50 kGy and is about 350% at 75 kGy. An interesting result is that the pentamethyl HALS (PMP and PMPM) have a higher stabilizing effectiveness on PP than that of the tetramethyl HALS (TMP and TMPM), that is, PMP has a higher stabilizing effectiveness than that of TMP, and PMPM has a higher stabilizing effectiveness than that of TMPM.

Tinuvin 622, Chimassorb 944, and GW-540 are the usually used marketable HALS; they are considered as some of the most effective HALS products. Compared to these HALS, PMPM also shows a higher stabilizing effectiveness in the irradiation of PP (Fig. 3). These results show that PMPM is an excellent stabilizer for improving the radiation resistance of PP.

Figure 4 shows that the  $E_b$  values of the PP-added PTMPM and PPMPM homopolymer samples separately versus different doses. It can be seen that the  $E_b$  values of these samples decrease very slowly with the dose; after 50 kGy irradiation, the  $E_b$  values are above 450%. This shows that both these homopolymers are very good light stabilizers in PP. Moreover, in this figure, we also can find that the pentamethyl HALS PPMPM has a higher stabilizing effectiveness than that of tet-



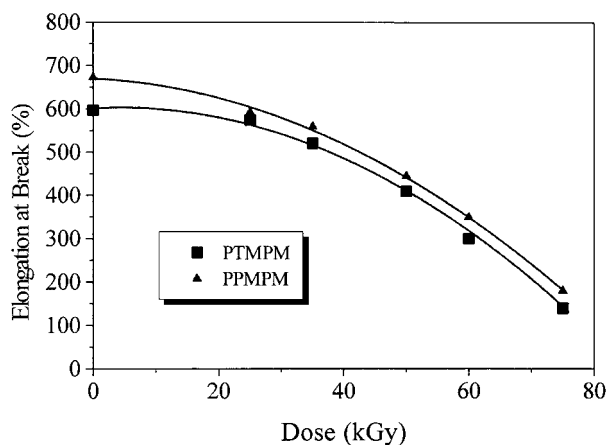


**Figure 3**  $E_b$  values of PP (MFI 1.8)-added Tinuvin 622, Tinuvin 770, Chimassorb 944, GW540, or PMPM versus dose.

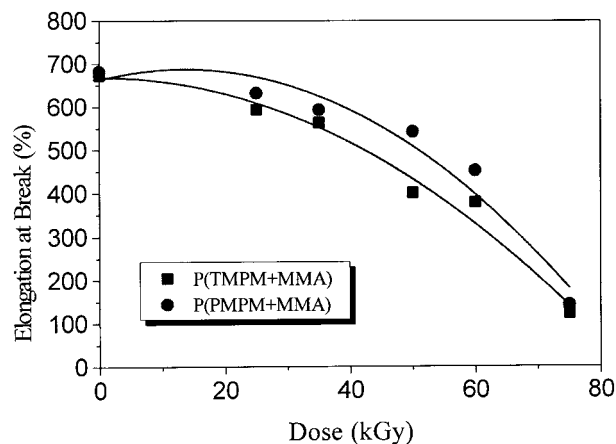
ramethyl HALS PTMPM, although the difference is not very significant.

The  $E_b$  values of PP-added P(TMPM + MMA) and P(PMPM + MMA), P(TMPM + MAA) and P(PMPM + MAA), P(TMPM + AA) and P(PMPM + AA) and P(TMPM + St) and P(PMPM + St) versus dose are shown, respectively, in Figures 5–8. The  $E_b$  values of all these PP samples are over 400% at 50 kGy; this shows that these polymeric tetramethyl or pentamethyl HALS are effective in improving the radiation resistance of PP. It can be seen from these figures that the copolymer series of the pentamethyl HALS also have a higher stabilizing effectiveness than that of those corresponding tetramethyl HALS.

The stabilizing effectiveness of HALS is affected by many factors, such as physical factors,

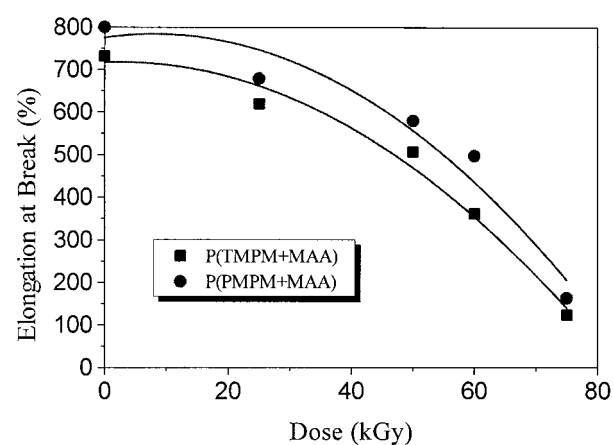


**Figure 4**  $E_b$  values of PP-PTMPM and PP-PPMPM versus dose.



**Figure 5**  $E_b$  values of PP-P(TMPM + MMA) and PP-P(PMPM + MMA) versus dose.

the chemical structure of HALS, and the existence of a synergism or antagonism effect with other additives. Physical factors are the important factors affecting the stabilizing effectiveness of HALS. The physical factors of HALS are their thermal stability, compatibility with the polymer they protect, solvent extraction resistance, etc. It can be seen from the results in Table I that the polymeric HALS have a much higher thermal stability than that of the LMW HALS; this is one of the reasons why polymeric HALS have a higher stabilizing effectiveness than that of LMW HALS. LMW HALS decompose and volatilize under thermal processing (about 200°C), so the effective concentration of HALS in the polymer decreases. However, the polymeric HALS do not or just a little decompose or volatilize under thermal pro-

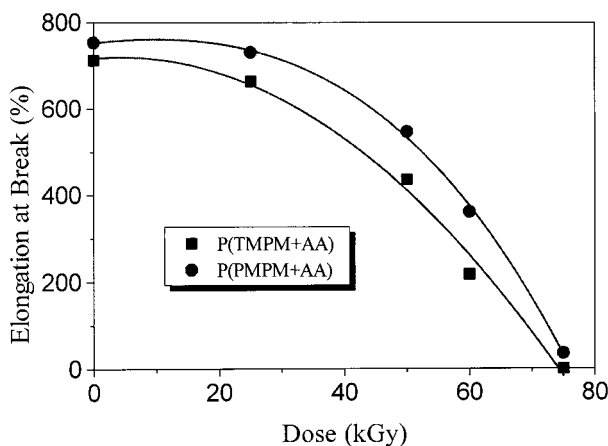


**Figure 6**  $E_b$  values of PP-P(TMPM + MAA) and PP-P(PMPM + MAA) versus dose.

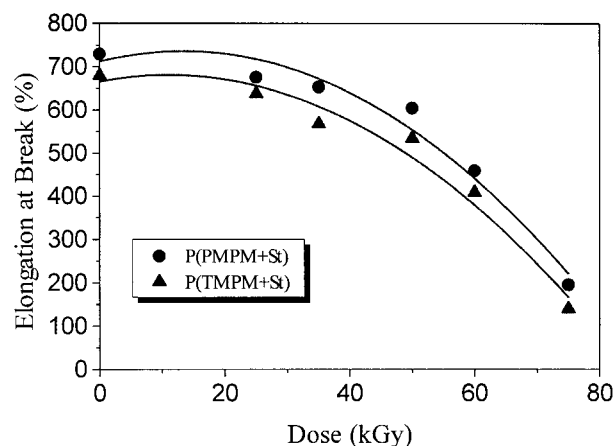
cessing. The solvent extraction resistance of polymeric HALS is better than that of LMW HALS (see Table II). The compatibility of polymeric HALS with the polymer is better than that of LMW HALS due to that the structure of polymeric HALS is more similar to that of the polymers they protected than that of LMW HALS, so the polymeric HALS show a higher stabilizing effectiveness than that of LMW HALS.

The extraordinary high stabilizing effectiveness of PMPM is a new discovery in this work. The LMW HALS liquid PMPM has a higher stabilizing effectiveness even than that of the polymeric HALS and marketable HALS. The high stabilizing effectiveness of PMPM can be explained as follows: First, PMPM is a liquid HALS with very good mobility; it can be dispersed more homogeneously in the polymer than can solid HALS (most of the HALS used are solid). Second, it is a reactive monomer; the existence of a double bond in PMPM also makes it possible to polymerize or graft on the PP chain under irradiation easily, as shown in Table III. This decreases its volatility and improves its compatibility with PP. This may be another reason for its high efficiency. These will benefit in increasing its thermal stability and compatibility with PP, so its stabilizing effectiveness increases.

The chemical structure of HALS is the essential important factor affecting its stabilizing effectiveness. That the pentamethyl HALS series has a higher stabilizing effectiveness than that of the tetramethyl HALS series was concluded in this work; the reason for their difference in stabilizing effectiveness is their difference in chemical structure. The pentamethyl HALS are tertiary amines,



**Figure 7**  $E_b$  values of PP-P(TMPM + AA) and PP-P(PMPM + AA) versus dose.



**Figure 8**  $E_b$  values of PP-P(TMPM + St) and PP-P(PMPM + St) versus dose.

and the tetramethyl HALS are secondary amines. It has been found that the pentamethyl piperidines are more effective in decomposing hydroperoxide<sup>8,9</sup> and quenching singlet oxygen<sup>10</sup> produced in polymers than are the tetramethyl piperidines. In these stabilizing reactions, tertiary amines are converted into secondary amines. Overall, pentamethyl HALS would have more stabilizing steps than would tetramethyl HALS. But there are conflicting reports concerning the performance of pentamethyl HALS as light stabilizers for polyolefins compared to the performance of the corresponding tetramethyl HALS.<sup>12,13</sup> The stabilizing mechanism of HALS in polyolefins under gamma irradiation will be studied in detail in further work.

## CONCLUSIONS

A new pentamethyl HALS 1,2,2,6,6-pentamethyl-4-piperidinyl methacrylate (PMPM) was synthesized and characterized. Its homopolymer and a series of copolymers were also synthesized. The thermogravimetry analyses show that LMW HALS (TMP, PMP, and TMPM) almost completely decompose under the thermal processing temperature, but the polymeric HALS show much higher thermal stability than that of LMW HALS. Polymeric HALS show better extraction resistance than that of LMW HALS, and part of the monomeric TMPM and PMPM in PP films can be polymerized when they are irradiated. The radiation resistance of PP-added HALS samples separately were evaluated by the  $E_b$  of the PP sam-

ples after different dose irradiations. PMPM shows a very high stabilizing effectiveness in comparison with other LMW HALS or polymeric HALS. The homopolymer and copolymers of PMPM are also good stabilizers for improving the

radiation resistance of PP. Both the tetra- and pentamethyl HALS are effective in radiation resistance. The pentamethyl HALS has a higher stabilizing effectiveness than that of tetramethyl HALS.

## APPENDIX

Trade Name	Supplier	Chemical Name	Structure
Tinuvin 770	Ciba-Geigy (Switzerland)	Bis(2,2,6,6-tetramethyl-4-piperidiny)l) sebacate	
Tinuvin 622	Ciba-Geigy (Switzerland)	Polymeric HALS	
Chimassorb 944	Ciba-Geigy (Switzerland)	Polymeric HALS	
GW-540	TCTRI <sup>a</sup>	Tris(1,2,2,6,6-pentamethyl piperidiny)l) phosphite	

<sup>a</sup> Taiyuan Chemical Technology Research Institute, Sanxi, China.

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