

# The Effect of Grafted TMPM on the Radiation Resistance of Polypropylene

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**ABSTRACT:** The  $\gamma$ -radiation-induced graft copolymerization of 2,2,6,6-tetramethyl-4-piperidinyl methacrylate (TMPM) onto polypropylene (PP) was investigated using a simultaneous-irradiation technique. The effects of solvents, atmospheres, dose, and monomer concentration on the percent of grafting were studied. The grafted TMPM showed better thermal stability, solvent extraction resistance, and compatibility with PP than monomeric TMPM or polymeric PTMPM. The stabilizing effectiveness of grafted TMPM on the radiation resistance of PP was found to be better than that of monomeric TMPM. The combination of grafted TMPM and low molecular weight hindered amine light stabilizers showed higher stabilizing effectiveness. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2150–2157, 1999

**Key words:** radiation-induced grafting; polypropylene (PP); hindered amine light stabilizer (HALS); radiation resistance

## INTRODUCTION

Polypropylene (PP) has become one of the largest and fastest growing plastics because of its versatility, wide applicability, and low cost, but some disadvantages in its properties have impeded its growth in commercial use. One of those is its poor stability to  $\gamma$ -irradiation. The use of  $\gamma$ -irradiation to sterilize plastic devices is increasing in popularity, but all plastics undergo some degradation as the result of irradiation. PP is particularly sensitive to radiation and it needs to be stabilized before use.<sup>1</sup>

Hindered amine light stabilizers (HALS) based on 2,2,6,6-tetramethylpiperidines are the most effective existing light stabilizers protecting polyolefines and other polymers from light-induced degradation.<sup>2</sup> They are also very effective in preventing PP from the damage of high-energy irradiation.<sup>3,4</sup> Low molecular weight (LMW) HALS

are unstable in the thermal processing of polymers and they have very low solvent extraction resistance, which leads to their very low stabilizing effectiveness.<sup>5</sup> Polymeric HALS are much more stable at high temperature than LMW HALS. Polymeric hindered amines are found to be good light stabilizers, but the stabilizing effectiveness of a macromolecular stabilizer is restricted by its poor compatibility with the polymer to be protected. An alternative approach to use a polymeric additive is to graft a copolymerizable stabilizer onto the polymer substrate.<sup>6</sup> This method can improve the compatibility of stabilizer with polymers and overcome the volatility problems. Allmer and coworkers<sup>7</sup> grafted glycidyl acrylate onto a polymer, then made it react with hindered amine with primary amine group, thus attaching HALS onto polymer. The grafting of HALS monomer with polymerisable double bonds directly onto polymer by  $\gamma$ -irradiation has not been reported.

Many vinyl monomers have been grafted onto PP by  $\gamma$ -radiation.<sup>8,9</sup> In the present investigation, the graft copolymerization of TMPM onto pow-

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dered PP was accomplished using a  $\gamma$ -ray irradiation technique. The thermal stability, extraction resistance, and compatibility of the grafted TMPM polymer were analyzed. In addition, the stabilizing effectiveness of grafted TMPM was measured.

## EXPERIMENTAL

### Materials

Anqing Petrochemistry Factory, Anhui, China, supplied powdered PP, melt flow index 1.8 g/10 min. It was Soxhlet-extracted with methanol for 48 h before use to remove all the soluble materials in it. TMPM (2,2,6,6-tetramethyl-4-piperidinyl methacrylate) was synthesized according to literature.<sup>10</sup> It was twice recrystallized from hexane before use. PTMPM was synthesized by radical polymerization. All the reagents used were of grade AR. Tinuvin 770 [Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate] was produced by Ciba-Geigy (Basel, Switzerland).

### Radiation Source

Irradiation of the samples was performed in a  $^{60}\text{Co}$  ( $3.7 \times 10^{14}$  Bq)  $\gamma$  chamber at room temperature. The dose rates were determined by a Fricke dosimeter.

### Grafting Procedure

Graft copolymerization was performed in a test tube in air or argon. A weighed amount of powdered PP and TMPM were put into a test tube, then solvent was added, and was left for 24 h to attain the equilibrium swelling of the powder. The tube was placed into the radiation chamber at a suitable distance and height for a desired period. The polymerization was stopped by the addition of a large volume of acetone to the reaction mixture. The whole mass was filtered and washed with acetone. The residual monomer and homopolymer were removed by Soxhlet extraction with methanol for 48 h. The graft copolymer was dried to constant weight under vacuum at 50°C. Percent grafting was calculated as follows:

$$\text{Percent Grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where  $W_g$  and  $W_0$  represent the weight of grafted and initial powdered PP, respectively.

### Thermogravimetry Analysis

The thermogravimetric analysis of PP grafted with TMPM or ungrafted was performed in the TG50 of a TA 3000 thermoanalysis system made by Mettler (Greifensee, Switzerland). Nitrogen was used as the purge gas at a flow rate of 15 mL/min and at a heating rate of 20 K/min. STEP analyses of every sample were performed. The TG and DTG curves of the samples were also obtained. The thermogravimetric analyses of TMPM and PTMPM were also performed and compared with grafted TMPM. Relative thermal stability of these samples was evaluated by comparison of the decomposition temperatures  $T_s$ ,  $T_{50}$ ,  $T_p$ , and  $T_e$ .  $T_s$  and  $T_p$  are the temperatures at which samples start to decompose and decompose most quickly, respectively;  $T_{50}$  and  $T_e$  are the temperatures at which samples undergo 50% and 100% decomposition.

### Extraction Resistance Test of HALS

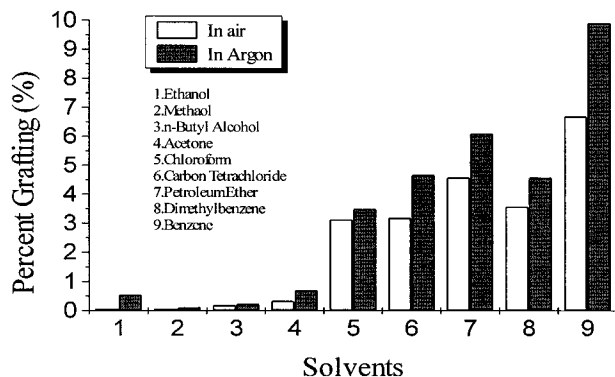
Four percent TMPM, PTMPM based on the weight of powdered PP were dissolved in alcohol separately. The solution was then mixed thoroughly with powdered PP with solvent removal under reduced pressure. The powdered PP mixed HALS and grafted TMPM were pressed into 100-mm thick films at 190°C. PP films containing HALS were Soxhlet-extracted using alcohol at various times. The weights of the PP film were measured before and after extraction using an M3 Microbalance (Mettler) with precision a of  $10^{-6}$  g. The material loss of HALS in PP film was calculated using the following equation:

$$\text{Material loss (\%)} = \frac{W_0 - W_t}{W_0} \times 100$$

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

### Scanning Electron Microscope Analysis of Grafted TMPM

The PP grafted TMPM (4.5% grafting) and powdered PP added 4.5% PTMPM were pressed into 100-mm thick films at  $190 \pm 5^\circ\text{C}$ . The film surfaces were analyzed using an X-650 scanning electron microscope (SEM) (Hitachi, Tokyo, Japan).



**Figure 1** Effect of solvent and atmosphere on the percent grafting of powdered PP.

### Preparation of Samples for the Test of Elongation at Break

HALS and other additives were mixed with powdered PP and extruded under  $200 \pm 5^\circ\text{C}$ , then heated under  $190 \pm 5^\circ\text{C}$  for 6 min and molded under pressure of  $1.47 \times 10^7$  Pa for 4 min and quenched immediately in tap water. The samples were punched into a dumbbell shape with a neck of 1 mm (thickness)  $\times$  3 mm (width). All the PP samples were irradiated 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 was evaluated by elongation at break (Eb) value. The higher Eb value of a PP sample at a given dose shows higher radiation resistance of PP. The stress-strain measurements of dumbbell samples, before and after different dose irradiation, were performed at a cross-head speed of 50 mm/min. The average Eb value of five samples was taken as the resultant value.

## RESULTS AND DISCUSSION

### Grafting of TMPM on PP

#### *Effect of Solvent and Atmosphere on Grafting*

Variation in the percent grafting in different solvents and atmospheres is presented in Figure 1. All the experiments were performed at a total dose of 25 kGy and a dose rate of 13.54 kGy/h. About 1 g PP, 0.2 g TMPM, and 1 mL solvent were used in each experiment.

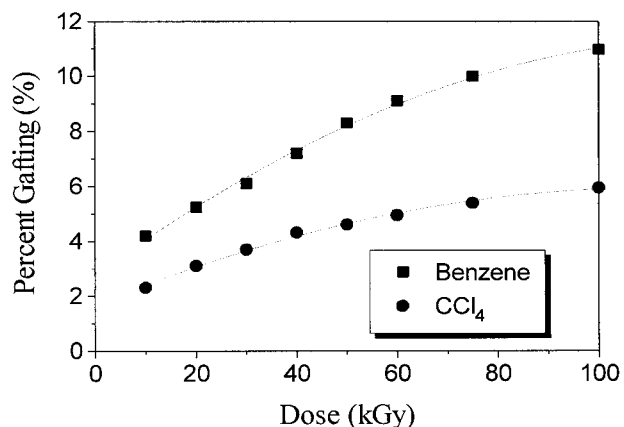
Figure 1 shows that the grafting was highly dependent on the nature of the solvent. The per-

cent grafting was much higher in benzene, dimethylbenzene, petroleum ether (b.p.  $60\text{--}90^\circ\text{C}$ ), chloroform, and carbon tetrachloride than that in methanol, ethanol, *n*-butyl alcohol, and acetone. The percent grafting was the highest when reactions were performed in benzene, whereas the percent grafting was very low when alcohol was used as the solvent.

PP is a nonporous material and it swells to some extent in organic solvents. Many solvents have been used in grafting experiments to enhance the accessibility of monomer to grafting sites within the polymer. The swell behavior of PP in several solvents has been studied.<sup>11,12</sup> It has been found that 10–12 h is required to attain equilibrium swelling. In our experiments, a period of 24 h was used to ensure enough swelling. It was observed that white powdered PP became semitransparent when swelled in benzene, dimethylbenzene, petroleum ether, chloroform, or carbon tetrachloride. However, this phenomenon was not observed in methanol, ethanol, *n*-butyl alcohol, and acetone. This showed that the degree of swelling in PP was much higher in the former solvents than those in the latter. The degree of the swelling of PP in solvent directly affected the percent grafting of TMPM onto PP. A conclusion therefore can be drawn experimentally that solvent is a very important factor in the radiation grafting of TMPM onto PP.

The effect of solvents on grafting may also be attributed to another factor, the stability of solvent under  $\gamma$ -irradiation. Benzene is a very stable reagent because of its  $\Pi$  bond structure, which can disperse radiation energy. Because the free radical yield of benzene is very low, it leads to a low degree of homopolymerization. Dimethylbenzene is not as stable in comparison with benzene; the two methyl groups in it can easily be attacked by  $\gamma$ -rays. This can result in the formation of more free radicals and the initiation of more homopolymerization. Alcohols, on the other hand, are unstable under  $\gamma$ -rays, which is the reason for the low percent grafting in them.

The grafting copolymerization in argon atmosphere was also studied. The reaction system was deaerated by bubbling argon gas for 8 min, then the test tube was sealed. The percent grafting was found to be higher in argon than in air. The oxygen molecules in air can participate in the formation of peroxy radicals, which initiate the homopolymerization of TMPM and leads to a low degree of grafting.



**Figure 2** Effect of total dose of irradiation on the percent grafting of powdered PP in benzene and CCl<sub>4</sub>.

### Effect of Total Dose on Grafting

The effect of total dose on grafting is shown in Figure 2. All the reactions were performed at a dose rate of 13.54 kGy/h. A total dose up to 100 kGy was used. About 1 g of PP, 0.2 g of TMPM, and 2 mL of solvent were used in each experiment.

It can be seen from Figure 2, that for all the grafting copolymerization performed in two different solvents, benzene and CCl<sub>4</sub>, the percent grafting initially increased linearly with dose. Beyond a certain dosage, the percent grafting appeared to level off. In the case of benzene, the percent grafting increased linearly from 10 to 60 kGy and leveled off beyond 60 kGy. In the case of CCl<sub>4</sub>, the percent grafting increased linearly from 10 to 50 kGy and leveled off beyond 50 kGy.

In the initial stage of polymerization, the monomer can diffuse easily to the active sites on powdered PP and the grafting copolymerization can take place smoothly. At the same time, homopolymerization also is not affected much. At the higher doses, more homopolymers are formed and the viscosity of the reaction solution becomes higher. Therefore, the homopolymer acts as a barrier against the monomer reaching the grafting sites on PP. This can result in a decrease in grafting and an increase in homopolymerization. As the grafting reaction processes, the monomer concentration of TMPM will decrease, which can also result in the decrease of percent grafting.

The percent grafting in benzene is higher than in CCl<sub>4</sub> at the same irradiation dose, and the dose at which percent grafting starts to level off is also higher in benzene. This is because of the higher

stability of benzene to  $\gamma$ -irradiation, resulting in less homopolymers formed in benzene than in CCl<sub>4</sub>.

### Effect of Monomer Concentration on Grafting

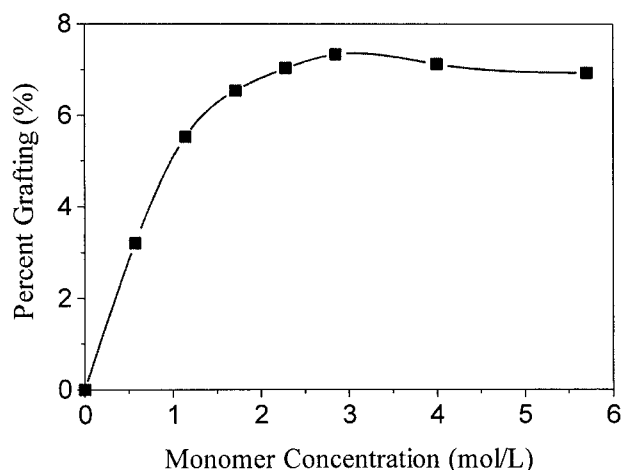
The effect of monomer concentration on percent grafting of TMPM onto PP using about 1 g of PP, 0–1 g of TMPM, and 2 mL of benzene at a dose rate of 13.54 kGy/h and at a constant total dose of 10 kGy is described in Figure 3.

The results show that the percent grafting increased with monomer concentration up to 2.85 mol/L. However, percent grafting increased significantly only up to 1.14 mol/L of monomer, beyond which the percent grafting increased very slowly. At a much higher monomer concentration, for instance 5.7 mol/L, the percent grafting tended to decrease.

In grafting, the rate of grafting is dependent on the PP macroradical yield and the monomer concentration in their vicinity. At a given dose rate, the PP macroradical yield is a fixed value. Therefore, the monomer molecule available in their vicinity is the decisive factor with grafting yield increases with monomer concentration in a limited range. However, as the monomer concentration increases, the homopolymerization of TMPM also increases, and beyond a certain value of monomer concentration, the rate of homopolymerization overpasses that of grafting with a leveling off and even decrease of percent grafting.

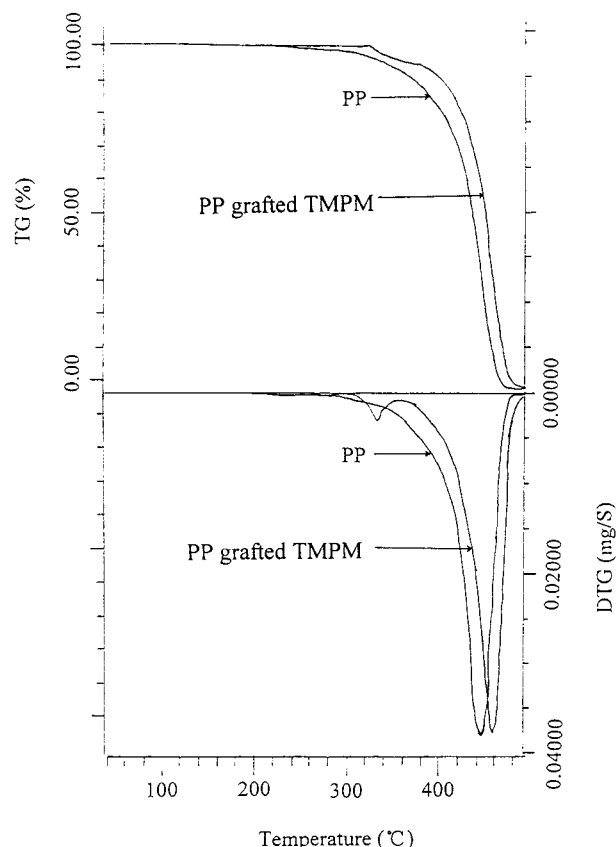
### Thermogravimetry Analysis of Grafted TMPM

The TG and DTG curves of PP and PP-grafted TMPM are shown in Figure 4. There is only one



**Figure 3** Effect of monomer concentration on the percent grafting of powdered PP.





**Figure 4** The TG and DTG curves of PP-grafted TMPM or ungrafted.

decomposition peak in the DTG curve of PP ungrafted TMPM,  $T_s$  is 200°C,  $T_p$  is 445°C, and  $T_e$  is 481°C. However, there are two decomposition peaks in the DTG curve of PP grafted TMPM—for the first decomposition peak,  $T_s$  is 233°C,  $T_p$  is 335°C, and  $T_e$  is 357°C; for the second decomposition peak,  $T_s$  is 357°C,  $T_p$  is 458°C, and  $T_e$  is 492°C. The material loss of the first decomposition peak obtained from step analysis is 4.3%, which is almost the same as the percent grafting (4.5%). Therefore, the first decomposition peak can be attributed to the decomposition of grafted TMPM. The second decomposition peak, on the other hand, can be attributed to the decomposition of PP.

The thermogravimetric analysis results of LMW HALS TMPM and its homopolymer PTMPM and the grafted TMPM are listed in Table I. It is well known that LMW HALS is unstable in thermal processing. TMPM starts to decompose at 97°C, at 179°C it decomposes to 50%, and at 207°C it decomposes completely. PTMPM shows much higher thermal stability than TMPM; it

**Table I**  $T_s$ ,  $T_{50}$ ,  $T_p$ , and  $T_e$  of HALS

HALS	$T_s$	$T_{50}$	$T_p$	$T_e$
TMPM	97	179	198	207
PTMPM	253	327	336	485
Grafted TMPM	233	324	335	

starts to decompose at 253°C, at 327°C it decomposes to 50%, and at 485°C it decomposes completely. The thermal decomposition of grafted TMPM is very similar to PTMPM. These results show that the grafted TMPM has much higher thermostability than LMW HALS TMPM. It does not decompose during thermal processing because its decomposition temperature is higher than the processing temperature. Therefore, the polymerization of HALS or grafting of HALS onto the polymer is an effective way to improve its thermal stability.

The decomposition peak temperature of PP grafted TMPM is about 10°C higher than that of PP ungrafted TMPM. The grafting of TMPM onto PP also increases the thermal stability of PP.

#### Extraction Resistance Test of HALS

The results of the solvent extraction resistance test of TMPM, PTMPM, and grafted TMPM are shown in Table II. LMW HALS TMPM can be very easily extracted from PP film by solvent. The weight loss reached above 60% after 2 h of extraction and about 90% after 16 h of extraction. These results showed that LMW HALS had very bad solvent extraction resistance. Polymeric HALS PTMPM showed better extraction resistance than TMPM. The material losses of polymeric HALS were lower than those of TMPM after 2 and 6 h of extraction, but they were very similar after 16 h of extraction, indicating that PTMPM cannot tolerate a long period of solvent extraction. Grafted TMPM exhibited excellent extraction resistance, showing no material loss even after long periods of extraction. Because grafted TMPM is grafted

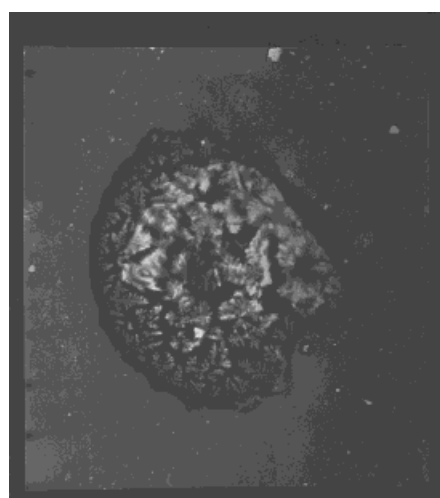
**Table II** Weight Loss of HALS in PP Film Extracted by Alcohol at Various Times

HALS	2 h (%)	6 h (%)	16 h (%)
TMPM	64	79	87
PTMPM	37	47	85
Grafted TMPM	0	0	0

on the PP matrix by chemical reaction, it can only be removed by breaking chemical bonds. On the other hand, HALS is physically added into PP and can be removed easily. Therefore, the grafting of TMPM onto PP is a good path to improve the extraction resistance of HALS.

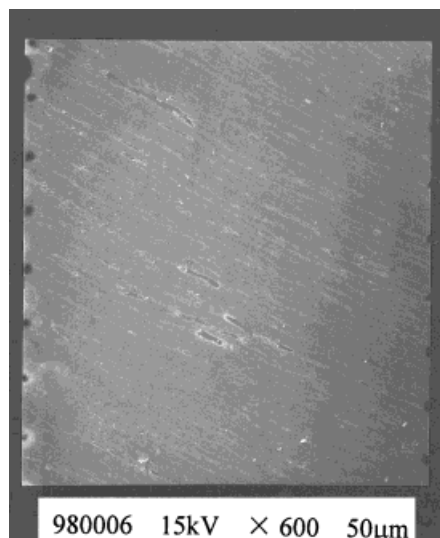
#### Compatibility of Grafted TMPM with PP

Figure 5 shows SEM microphotos of film surface of PP added PTMPM (4%) and PP grafted TMPM (percent grafting 4.3%). The SEM analysis indi-



980020 15kV × 600 50μm

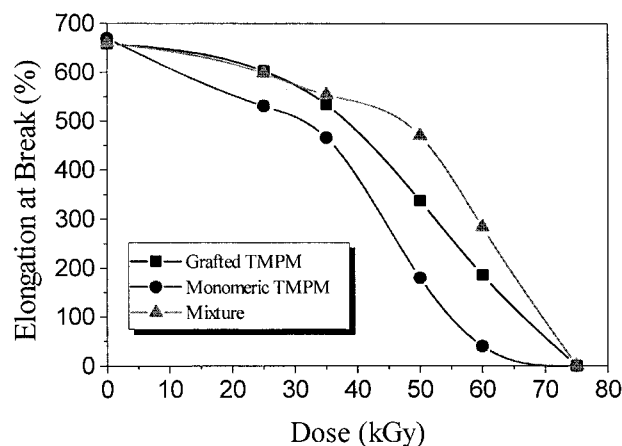
(a)



980006 15kV × 600 50μm

(b)

**Figure 5** SEM microphotos of film surface of PP added PTMPM (a) and PP grafted TMPM (b).



**Figure 6** The change of Eb of PP-added grafted TMPM, monomeric TMPM, or the mixture with irradiation dose.

icates that the compatibility of grafted TMPM with PP is better than that of PTMPM with PP. This shows that radiation-induced grafting of HALS monomers onto polymer is a good method to improve its compatibility with polymers.

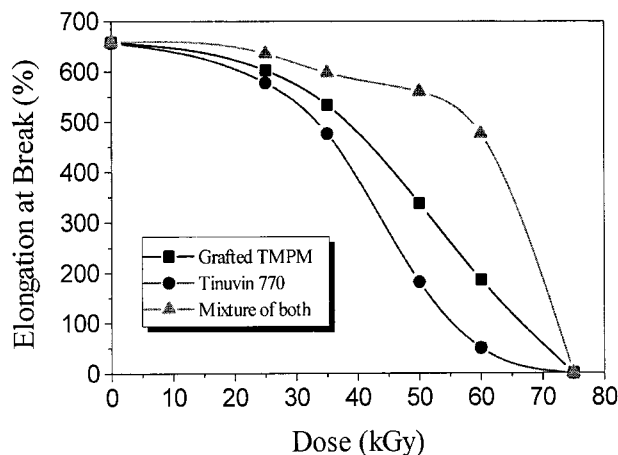
All these analysis results show that grafted TMPM has better thermal stability, solvent extraction resistance, and compatibility with polymer than LMW HALS or polymeric HALS. The grafting of TMPM onto PP is a very good way to increase its thermal stability, solvent extraction resistance, and compatibility with polymer, thus increasing its stabilizing effectiveness.

Although the grafting of HALS monomer TMPM onto PP is only discussed in this work, the grafting of other stabilizers with polymerisable double bonds onto polymers should also be feasible.

#### Radiation Resistance Test of PP-Added Grafted TMPM

The powdered PP grafted TMPM was added into PP as a light stabilizer. The content of TMPM in graft copolymer was calculated according to percent grafting. The weight of TMPM in grafted TMPM and the monomeric TMPM added in PP were 0.1% of the weight of PP. These PP samples were irradiated and tested under the same conditions.

From Figure 6, it can be seen that the PP sample added-grafted TMPM has better radiation resistance than the PP sample added monomer TMPM. The Eb value of the PP sample added-grafted TMPM was 400% after 50 kGy of irradi-



**Figure 7** The change of Eb of PP with irradiation dose.

ation and 230% after 60 kGy of irradiation. The Eb value of the PP sample added monomeric TMPM was 200% after 50 kGy of irradiation and close to 0 after 60 kGy of irradiation. This result proves that the grafting of LMW HALS TMPM onto PP is a feasible way to increase its stabilizing effectiveness.

The grafted TMPM used in the experiments above was only the pure grafted copolymer. The homopolymer PTMPM produced in grafting copolymerization and unreacted monomeric TMPM were extracted by alcohol from the mixture of grafting product and by-product, etc. If the homopolymer PTMPM and unreacted TMPM were not extracted, the mixture of grafted TMPM, homopolymer PTMPM, and monomeric TMPM showed higher stabilizing effectiveness than pure grafted TMPM (see Fig. 6). In this case, polymeric and LMW monomeric light stabilizer are included in the mixture. In another experiment, grafted TMPM (0.03% of the weight of PP) and Tinuvin 770 (0.07% of the weight of PP) were added to PP. To compare the combination effect of the grafted TMPM and Tinuvin 770, the PP samples with grafted TMPM or with Tinuvin 770 were also prepared. All samples were prepared, irradiated, and tested under the same conditions. The results are shown in Figure 7.

The combination of grafted TMPM and LMW HALS Tinuvin 770 showed much higher stabilizing effectiveness than grafted TMPM or Tinuvin 770 used alone. The PP sample with a mixture of grafted TMPM and Tinuvin 770 showed very good radiation resistance; its Eb value was about 500%

even after 60 kGy of irradiation. The Eb value of PP added with TMPM alone was about 200% and that of PP with Tinuvin 770 was close to 0 after 60 kGy of irradiation.

As discussed previously, the grafting of TMPM onto PP increases its thermal stability, extraction resistance, and compatibility and, in turn, its stabilizing effectiveness increases. However, the grafting of TMPM onto PP has one drawback—low mobility; this drawback can affect its stabilizing effectiveness. On the other hand, LMW HALS has good mobility and can be dispersed homogeneously in PP. It, however, does not have good thermal stability, extraction resistance, and compatibility with polymers. When the grafted TMPM and LMW HALS are used together, the LMW HALS overcomes the low mobility drawback of grafted TMPM with an increase in overall stabilizing effectiveness.

From the results obtained above, a conclusion can be drawn that the combination of grafted TMPM and LMW HALS shows higher stabilizing effectiveness. A hypothesis can then be forwarded that the combination of polymeric and LMW stabilizer shows higher stabilizing effectiveness.

## CONCLUSION

The effects of various grafting conditions on the percent grafting were studied. It was shown that percent grafting in benzene,  $\text{CCl}_4$ , and petroleum ether were higher than that in other solvents. The percent grafting was higher in argon atmosphere than in air when graft copolymerization was performed. For the grafting copolymerization performed in benzene, the percent grafting increased linearly from 10 to 60 kGy and leveled off beyond 60 kGy. In  $\text{CCl}_4$ , the percent grafting increased linearly from 10 to 50 kGy and leveled off beyond 50 kGy. Percent grafting also increased continuously with the increase of monomer concentration up to 2.85 mol/L, but significant increase in grafting was observed only up to 1.14 mol/L.

The thermal stabilization, resistance to solvent extraction, compatibility with PP of grafted TMPM, is better than monomeric TMPM or PTMPM.

The stabilizing effectiveness of grafted TMPM on the radiation resistance of PP was found to be better than that of TMPM monomer. The mixture of grafted TMPM and LMW light stabilizer had higher stabilizing effectiveness than any of the components.

These results show that grafting HALS monomers on polyolefines is a good method of increasing the thermal stabilization, resistance to solvent extraction, compatibility with polyolefines, and radiation resistance of polyolefines. This method is very useful in practice.

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