Effect of Stabilizer on the Radiation Grafting of Methylmethacrylate onto Polypropylene

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ABSTRACT: The effects of the molecular weight of polypropylene, nucleating agent, and types of stabilizers on the grafting of methylmethacrylate onto polypropylene sheets were examined. The oxidation of polypropylene sheet surfaces exposed to air after irradiation was studied by measuring survey scan spectra with an X-ray photoelectron spectrometer (XPS). The 1,1-diphenyl-2-picrylhydrazyl (DPPH) technique was utilized to evaluate the concentration of peroxide formed on the irradiated polypropylene sheet by counting the quantity of DPPH consumed by the reaction of peroxide radicals with DPPH. Plastics stabilizers caused a decrease in the concentration of peroxide in the polymer as well as trapped radicals. It was shown that the stabilizer in polypropylene markedly decreased the grafting of methylmethacrylate onto polypropylene. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2323–2330, 1998

INTRODUCTION

The radiation-induced graft polymerization of monomers onto polymer substrates has been studied with various monomers and polymers. Radiation grafting has aroused considerable interest because it offers various techniques to impart desirable properties to polymers, without significantly affecting its original properties.[1–5]

The utilization of simple additives to enhance the grafting yields at particular doses has received considerable attention. In particular, the addition of mineral acid increases the radiation grafting yields.[6,7] In a further development of the additive effect, polyfunctional monomers[8,9] have been found to be useful at enhancing radiation grafting yields when used in additive amounts in the monomer solution. Certain metallic salts are currently used in a wide range of radiation polymerization processes. In some cases, they accelerate the rate of reaction. For example, in grafting, they increase the grafting yield and reduce homopolymerization. These concepts are of economic significance in commercial processing since lower radiation doses are required to produce a given product.

Most polymers are susceptible to oxidative degradation. In particular, polymers formed by chain reaction polymerization are more sensitive to oxidative degradation. Therefore, some polymer substrates contain various additives, such as antioxidants and ultraviolet (UV) stabilizers.[10–12] It is possible to assume that the additives in polymers influence the grafting yield because they have a strong radical scavenging function. Until now, there have been no articles concerned with the effect of stabilizers on the radiation grafting yield. The present experiments aim to study the

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Table I Molecular Weight of Polypropylene

Sample No.	Polymer	$M_n \cdot 10^{-4}$	$M_w \cdot 10^{-4}$
1	Homo polypropylene (Homo-PP)	60	30
2	Homo polypropylene (Homo-PP)	55	28
3	Homo polypropylene (Homo-PP)	42	20
4	Propylene copolymer (Co-PP)	63	24
5	Propylene terpolymer (Ter-PP)	80	30

effect of stabilizers on the grafting yield of methyl methacrylate onto polypropylene. The effects of the molecular weight of polypropylene, nucleating agents, and the types of stabilizers and polypropylene on the grafting yield were also examined.

EXPERIMENTAL

Materials

Commercial polypropylene, propylene copolymer having 3% ethylene units, and propylene terpolymer having both 3% ethylene and 4% 1-butene were obtained from the Honam Petrochemical Corp. (Table I). Irganox1076 [3,5-bis (1,1-dimethyl-ethyl)-4-hydroxy-octadecyl ester] was used as an antioxidant. The UV stabilizer in this experiment was Tinuvin770(2,2,6,6-tetramethyl-4-piperidyl sebacate). Methyl methacrylate (Junsei Chemical Co., Ltd.) was used without further treatment. Other chemicals were reagent grade.

Preparation of Sample

Polypropylene samples (4 × 4 × 5 cm) were prepared by injection molding after mixing polypropylene of various molecular weights, propylene copolymer, and propylene terpolymer in the presence or absence of a stabilizer and nucleating agent, respectively.

Irradiation and Determination of Peroxide

Samples were irradiated with Co-60 at a dose of 30 kGy and exposure rate of 0.729 kGy/h in the presence of air. The oxidation degree of polypropylene by irradiation was analyzed with electron spectroscopy for chemical analysis (ESCA) with a V. G. Scientific ESCALAB MKII spectrometer using MgK α X-ray radiation at 1253.6 eV operating at 10^{-9}mbar and a photoelectron take-off angle of 60°. Polypropylene including and excluding Tinuvin 770 was cut to form 6-mm disks and then introduced into the UHV spectrometer chamber. MgK α radiation was used with the analyzer operating at a constant band pass energy of 20 eV. The spectrometer was calibrated by assuming binding energy of the Au $4f_{7/2}$ line to be 83.9 eV with respect to the Fermi level. Survey scans (0 to 1200 eV) were recorded for each sample to obtain a qualitative elemental analysis.

For the irradiated samples, the amount of peroxide formed around the surface was quantified with 1,1-diphenyl-2-picrylhydrazyl (DPPH).[13] The polypropylene samples stored at room temperature for 10 days after irradiation were dipped into a DPPH–tolune solution (1×10^{-4} mol/L) at 70°C for 3 h to decompose the peroxides formed on and near the polypropylene surfaces. The DPPH molecules consumed were measured from the difference in transmittance between the control and irradiated polypropylene samples at 520 nm using a spectrophotometer (Cesil Instruments, CE 292).

Grafting Procedure

The polypropylene samples stored at room temperature for 10 days after irradiation were used for the peroxide-induced grafting reaction, while the polypropylene samples stored in a refrigerator kept at −130°C immediately after irradiation were used for the grafting process using trapped radicals. The grafting experiments were performed in a glass ampoule having a cock, with the solvent and additives being added first, followed by the monomer. The irradiated polypropylene sample was immersed in the monomer solution and then purged by bubbling nitrogen. The grafting reaction was carried out by placing the ampoules in a water bath set at the relevant temperature. After the grafting reaction, the grafted samples were taken out of the monomer solution in glass ampoules and washed with acetone to remove the remaining homopolymer.

The degree of grafting was determined as follows:

$$\text{Degree of grafting } (\%) = \frac{W_g - W_0}{W_0} \times 100$$

where W_0 and W_g are the weights of the polypropylene samples before and after grafting, respectively.

RESULTS AND DISCUSSION

Among the synthetic polymers, polypropylene is widely used because of its growing commercial applications. The backbone of polypropylene has a hydrogen atom on a tertiary carbon atom, and it is well known that this tertiary hydrogen atom is involved in the degradation of a macromolecular chain. Various kinds of stabilizers are contained in polypropylene to prevent the oxidative degradation during processing steps and UV degradation. It is important to examine the effect of the stabilizer, the type of stabilizer, and the difference of the polypropylene molecular weights on the grafting reaction in order to get the required grafting yield with lower radiation doses.

The methods of achieving a graft reaction using radiation can be divided into simultaneous irradiation and preirradiation. In this study, a preirradiation grafting method was used. A preirradiation grafting technique is favorable from the viewpoint of forming less homopolymer. When organic polymers are subjected to ionizing radiation, the trapped radicals or macromolecular peroxide and hydroperoxides capable of initiating a graft copolymerization reaction are generally formed. The hydrogen atom on the tertiary carbon atom is extremely reactive, and the site for the reaction with oxygen to form hydroperoxide, upon decomposition, results in free radicals required for graft polymerization. The mechanism of peroxidation in polypropylene has been studied in detail by Chapiro.[14] When such polymeric peroxides are used to initiate a graft copolymerization reaction, diperoxides generate only a graft copolymerization, while hydroperoxides lead to an equivalent amount of graft polymers and homopolymers. The thermal decomposition of the diperoxide produces $PO^{\bullet}$ radicals, while hydroperoxide produces $PO^{\bullet}$ radicals and $OH^{\bullet}$ radicals. These radicals initiate the grafting reaction.

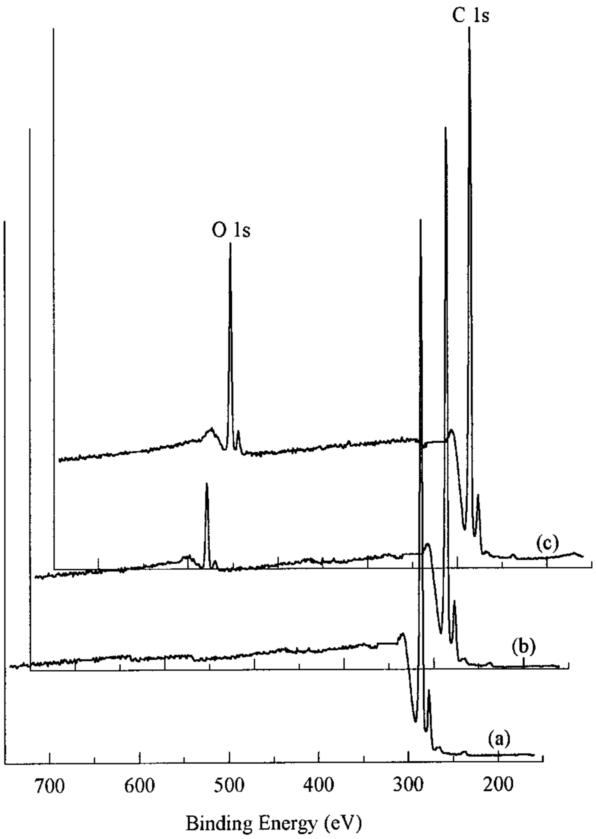

Figure 1 ESCA survey scan spectra of (a) control, (b) polypropylene immediately after irradiation, and (c) polypropylene stored in the room temperature during 10 days after irradiation.

The oxidation of the polypropylene sheet surfaces exposed to air after irradiation was studied by measuring survey scan spectra with an X-ray photoelectron spectrometer (XPS). A comparison of the oxidation behavior of 20×10^4 molecular weight polypropylene with and without 0.1% Tinuvin 770 after irradiation is presented in Figures 1 and 2. Figure 1 shows the ESCA survey scan spectra of polypropylene sheet surfaces without Tinuvin 770. As shown in Figure 1, the irradiated polypropylene had oxygen (O-1s : 537.0 eV) peaks as well as carbon (C-1s : 284.6 eV) peaks, with there being no oxygen peak for unirradiated polypropylene. The oxygen peak of polypropylene immediately after irradiation was lower than that of polypropylene stored at room temperature for 10 days after irradiation due to the increased amount of carbonyl groups on the polypropylene surfaces. Whereas in the case of polypropylene with Tinuvin 770, it was shown that all samples had oxygen peaks because Tinuvin 770 has 2 car-

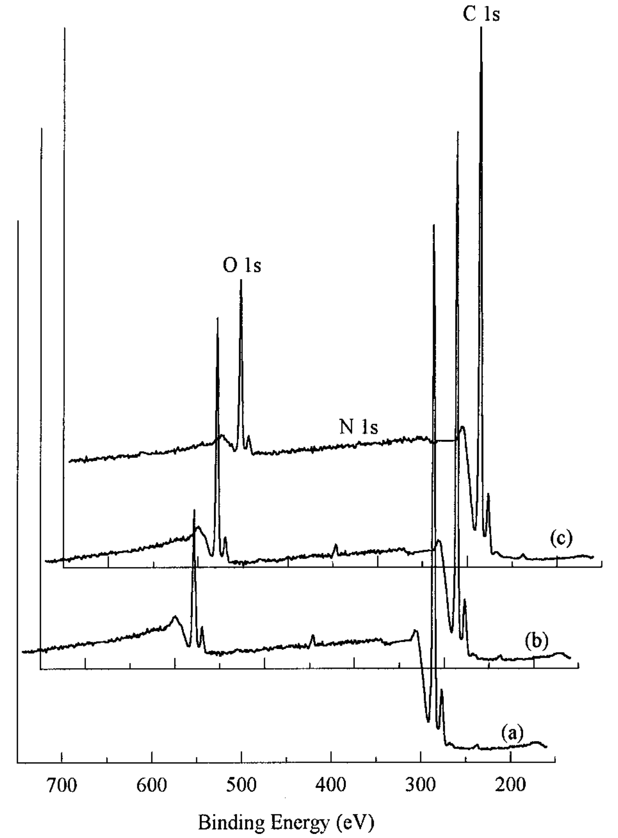

Figure 2 ESCA survey scan spectra of polypropylene including Tinuvin 770 (0.1%) of (a) control, (b) polypropylene immediately after irradiation, and (c) polypropylene stored in the room temperature during 10 days after irradiation.

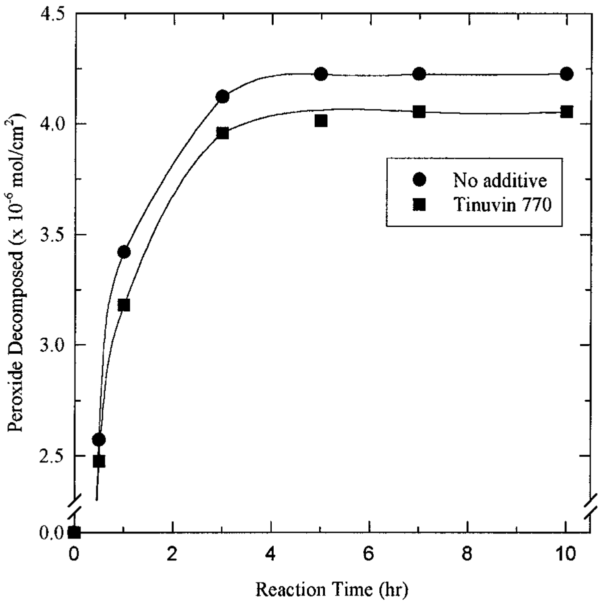

Figure 3 Decomposition of peroxides at 70°C in toluene for the peroxidized polypropylene (molecular weight = 28 × 10^4).

bonyl bonds by themselves. Oxygen bands increased immediately after irradiation, then decreased during storage after irradiation. It may be explained that the inclusion of Tinuvin 770 in the polypropylene affectively scavenges the oxide radicals remaining after irradiation. The oxygen atomic percentage calculated from the peak areas of the ESCA survey scan is shown in Table II.

The DPPH technique was utilized to evaluate the concentration of peroxide formed on the irradiated polypropylene sheet by counting the quantity of DPPH consumed from the reaction of peroxide radicals with DPPH. Figure 3 shows the decomposed peroxide concentration calculated from the DPPH consumption as a function of the

Table II ESCA Analysis of Polypropylene Sheet Surfaces

Polypropylene		Atomic (%)[c] Carbon	Oxygen	Ratio[a] —C—O—/—C—C—
No additive	Control	99.987	0.013	—
No additive	Irradiation[a]	91.282	8.718	0.154
No additive	Oxidation[b]	86.328	13.672	0.442
Tinuvin 770 (0.1%)	Control	88.749	11.251	0.362
Tinuvin 770 (0.1%)	Irradiation[a]	79.017	17.752	0.711
Tinuvin 770 (0.1%)	Oxidation[b]	85.283	11.484	0.380

[a] Polypropylene immediately after irradiation.
[b] Polypropylene stored at room temperature for 10 days after irradiation.
[c] Analyzed from survey scan spectra.
[d] Analyzed from carbon 1's core level spectra.

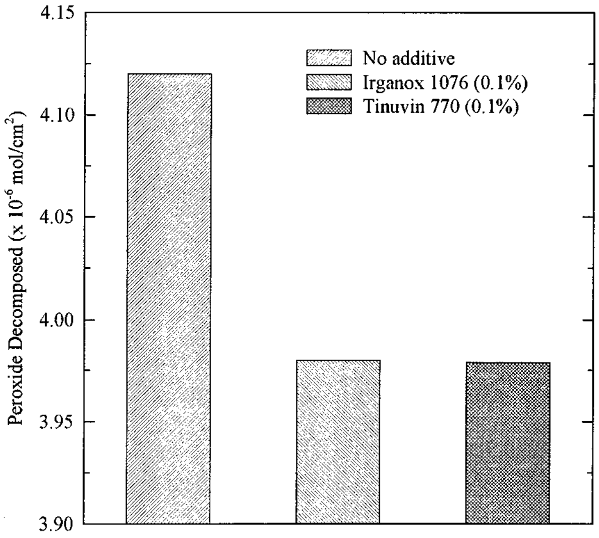

Figure 4 Decomposition of peroxides at 70°C in toluene for the peroxidized polypropylene (molecular weight = 20×10^4).

reaction time at 70°C for a polypropylene sheet irradiated by γ-rays at the dose of 30 kGy. The decomposition of peroxides continued up to 5 h and then leveled off. Therefore, the concentration of peroxide formed in the irradiated polypropylene was determined after decomposing the peroxides in DPPH solution at 70°C for 5 h. Figure 4 shows the peroxide concentration after polypropylene samples containing Irganox 1076 and Tinuvin 770 were irradiated. Irganox 1076 is a hindered phenol used for antioxidant, and Tinuvin 770 has been used as an effective UV stabilizer. The reason why the peroxide concentration in polypropylene with these additives is low can be attributed to the combination of the above stabilizer with radicals formed by γ-ray irradiation. Propagation of radicals may be prevented if the radical abstracts a hydrogen atom from the stabilizer during a chain transfer process. Also, a stabilizer effectively scavenges the radicals formed during radiation, as shown in Figure 2. The effect of the type of stabilizer on the concentration of peroxide was negligible (Fig. 4).

Figure 5 shows the peroxide concentration formed in the polymer after polypropylene with a different molecular weight was irradiated by γ-rays. Polypropylene of high molecular weight had the smaller peroxide concentration. This result is coincident with the fact that lower-molecular-weight polypropylene degrades markedly with increasing doses compared to the high-molecular weight polypropylene.[15] With the addition of Tinuvin 770, 3 polymers lead to a low peroxide concentration.

Polypropylene, propylene copolymer, and propylene terpolymer were irradiated to confirm their peroxide concentrations after irradiation (Fig. 6). The peroxide concentration of homopolymers in the absence of Tinuvin 770 was comparatively higher than those of propylene copolymers and propylene terpolymers. On the other hand, the peroxide concentration of homopolymers in the presence of Tinuvin 770 was comparatively lower than that of propylene copolymers and propylene terpolymers. It can be explained that the addition effect of a stabilizer in propylene copolymers and propylene terpolymers on the peroxide concentration was not high. Figure 7 shows the effect of Tinuvin 770 concentration on the peroxide content formed on the polypropylene. The peroxide concentration of polypropylene decreased with increased Tinuvin 770. This means that Tinuvin 770 effectively scavenges the radicals formed during irradiation or after irradiation.

A nucleating agent is added to improve the transparency of polypropylene. This property is desirable in producing medical disposable products. The effect of various nucleating agents on the peroxide concentration of polypropylene was shown in Figure 8. The nucleating agents, such as sebacic acid, 1,3,2,4-di(ethylbenzylidene)sobitol, dibenzylidenesorbitol, bis(p-methyl benzylidene)-

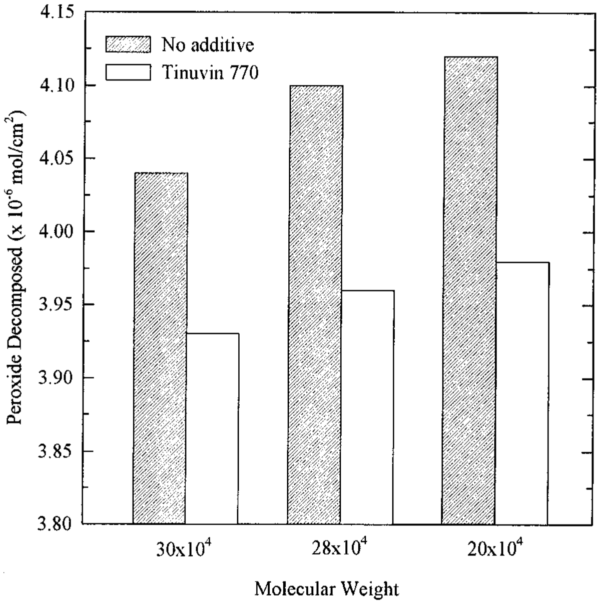

Figure 5 Decomposition of peroxides at 70°C in toluene for the peroxidized polypropylene with different molecular weights.

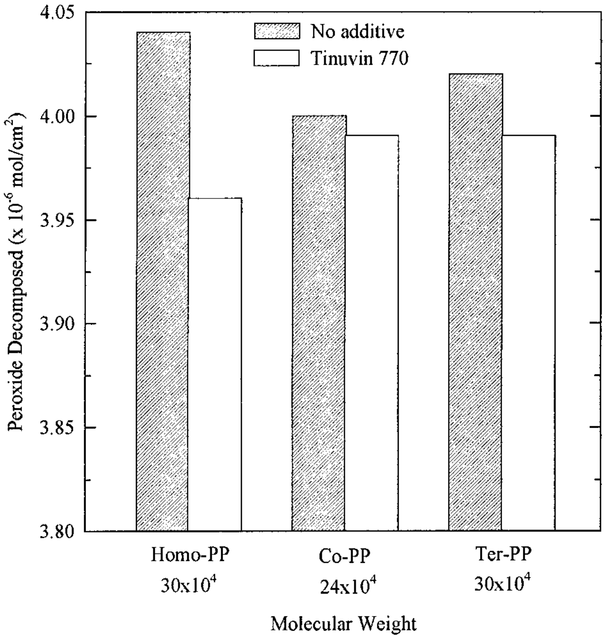

Figure 6 Decomposition of peroxides at 70°C in toluene for the peroxidized polypropylene.

sorbitol, ter-butyl benzoic aluminum, and sodium benzoate, were used. The addition of a nucleating agent led to an increase in peroxide concentration. This result coincides with the chemiluminescence analysis of irradiated polypropylene, where polypropylene with a nucleating agent is more oxidized than polypropylene without nucleating agent.[16]

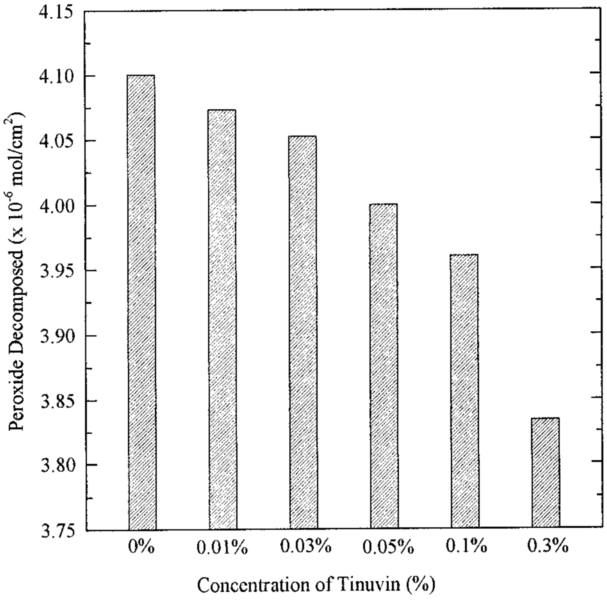

Figure 7 Decomposition of peroxides at 70°C in toluene for the peroxidized polypropylene with Tinuvin 770 (polypropylene molecular weight = 28 × 10^4).

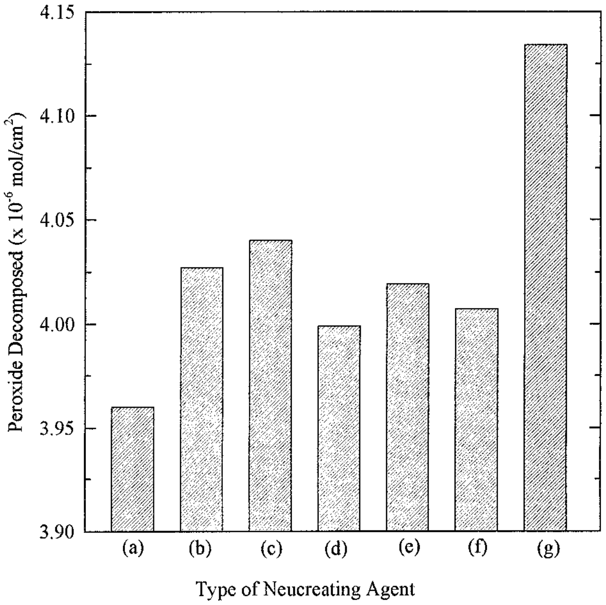

Figure 8 Decomposition of peroxides at 70°C in toluene for the peroxidized polypropylene, including (a) tinuvin 770, and Tinuvin 770 with (b) sebacic acid, (c) 1,3,2,4-di(ethylbenzylidene)sorbitol, (d) dibenzylidenesorbitol, (e) bis(*p*-methyl benzylidene)sobitol, (f) terbutylbenzoic aluminum, and (g) sodium benzoate (polypropylene molecular weight = 28 × 10^4).

Figure 9 shows the effect of a stabilizer on the peroxide-induced grafting reaction of methyl methacrylate onto 20 × 10^4 molecular weight polypropylene. The radiation grafting reaction was carried out at 70°C to evaluate the grafting reaction induced by the decomposition of peroxide formed in each polymer during the 10 days after irradiation. As expected, the grafting yield of polypropylene decreased considerably with the addition of a stabilizer. It was confirmed that this graft reaction at 70°C is induced by the decomposed peroxide radicals formed by heating because it did not proceed at 50 or 30°C, where a graft reaction is possible by trapped radicals. The reason for the low grafting yield in polymers with a stabilizer can be attributable to the low concentration of peroxide in the polymer by the presence of a stabilizer in the polymer.

Homopolypropylene of different molecular weights was grafted with methyl methacrylate using peroxide-induced grafting (Fig. 10). Polypropylene of high molecular weight had the smaller grafting yield because it had the lower peroxide concentration, as shown in Figure 5.

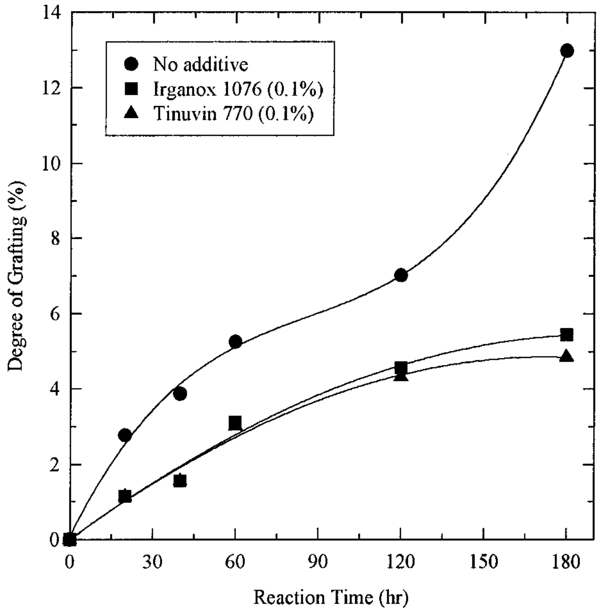

Figure 9 The effect of stabilizer on the peroxide-induced grafting of methyl methacrylate onto 20 × 10^4 molecular weight polypropylene.

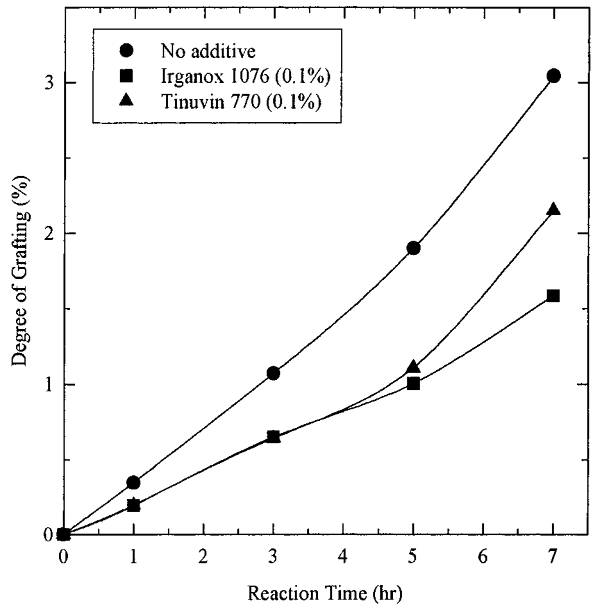

Figure 11 The effect of stabilizer on the trapped radical-induced grafting of methyl methacrylate onto 20 × 10^4 molecular weight polypropylene.

It is known that free radicals created by irradiation in solid polymers are immobilized and may remain trapped for a considerable length of time. The major factor governing the trapping of radicals is the physical state of the irradiated polymer. The important factor influencing the trapping of radicals is the physical state of the irradiated polymer, such as the degree of crystallinity, the molecular weight distribution, and the main chain mobility. To examine the effect of a stabilizer on the grafting reaction by trapped rad-

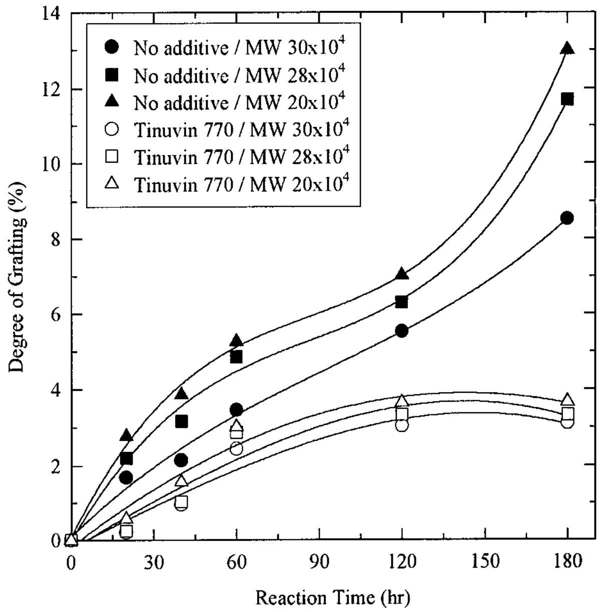

Figure 10 The effect of molecular weight on the peroxide-induced grafting in the presence or absence of stabilizer.

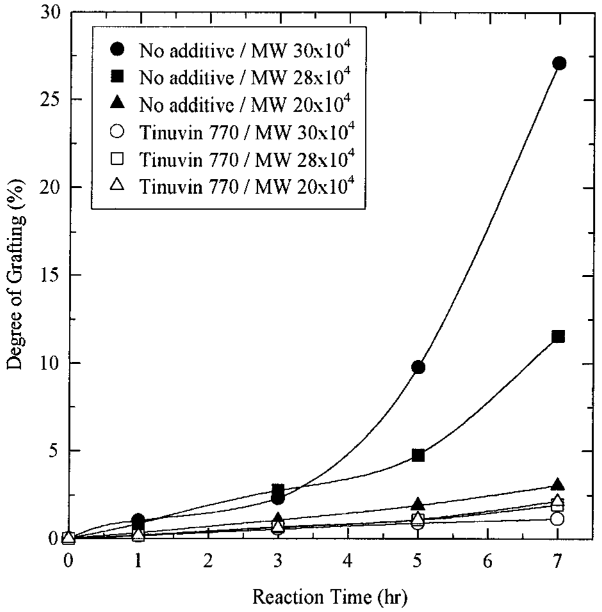

Figure 12 The effect of molecular weight of polypropylene on the trapped radical-induced grafting yield.

icals, polypropylene with a molecular weight of 20 $\times 10^4$ was used for the grafting reaction immediately after irradiation (Fig. 11). The grafting yield in this grafting condition has the same trend as the grafting system induced by the dissociation of peroxide. These results confirm that the addition of a stabilizer in polypropylene leads to a reduction of trapped radicals in polypropylene.

The higher the molecular weight of polypropylene is, the less mobile the molecular chain of polypropylene is. Therefore, it is possible to consider that the lifetime of trapped radicals in high-molecular-weight polypropylene is longer than that of low-molecular-weight polypropylene. Therefore, higher-molecular-weight polypropylene is more effective to the grafting reaction using trapped radicals, as shown in Figure 12. A polymer having a high molecular weight is beneficial to the preirradiation grafting reaction.

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