

Synthesis and Properties of New Polymer Having Hindered Phenol Antioxidants

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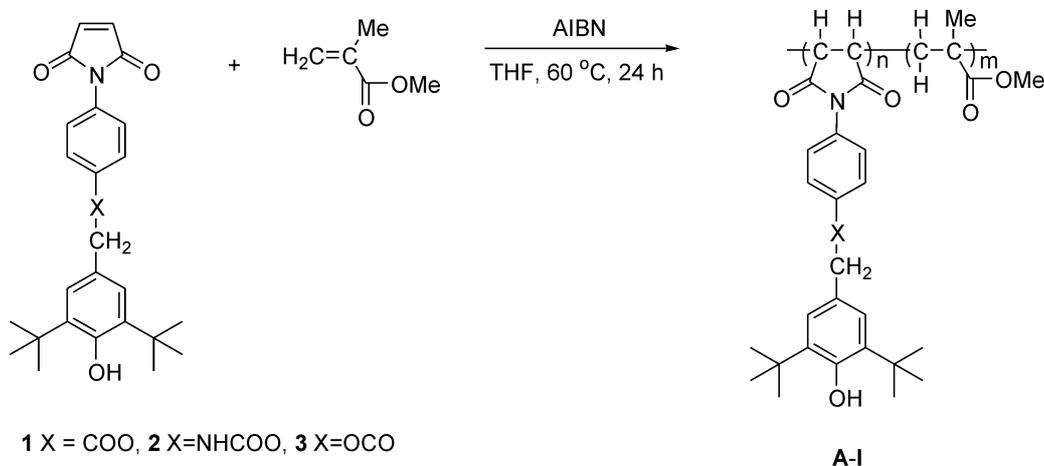
It is well known that the addition of antioxidants is the most convenient and effective way to block the thermal oxidation of polyolefins. Hindered phenol antioxidants, which contain the 2,6-di-*tert*-butylphenol functional group, are very effective primary antioxidants.^{1,2} However, low molecular weight (MW) antioxidants are easily lost from the polymers by the physical loss such as migration, evaporation, and extraction by liquid. The effectiveness of low MW antioxidants is limited. Therefore a new trend for antioxidant development is to prepare antioxidant with higher MW.^{3,4} The copolymerization or homopolymerization of the functional monomer bearing hindered phenol antioxidants is a conventional method for preparing polymeric antioxidants. Thus the preparation of functional monomer containing hindered phenol is a very important initial step. Several monomeric antioxidants have been reported, mostly they are based on the derivatives of acrylate.⁴ Recently we reported the synthesis and homopolymerization of hindered phenol antioxidants containing a polymerizable maleimide group.⁵ In this paper, as a part of this work, the synthesis of copolymers containing hindered phenol and the examination of their antioxidative effects are disclosed (Scheme 1).

Experimental Section

General. The reagent grade chemicals were purchased from Aldrich Co. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature. All solvents were reagent grade. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl.

¹H NMR spectra were recorded on a 300 MHz spectrometer; chemical shifts are reported in ppm using TMS as internal standard. IR spectra were recorded on a Nicolet FT IR spectrometer.

Copolymerization of Monomeric Antioxidants. A general radical copolymerization procedure was as follows: A mixture of monomeric antioxidant (1.00 g), methyl methacrylate (MMA), and AIBN (2 wt %, based on the weight of the monomeric antioxidants) was dissolved in THF (1 mL) and heated at 60 °C under nitrogen for 24 h. A polymer formed was dissolved in dichloromethane and poured into methanol. The precipitated polymer was collected and dried under vacuum to give the desired copolymer. The polymers were fully characterized by spectroscopy and TGA. Molecular weights of the polymers were measured by GPC in THF and inherent viscosities were measured with viscosity tube in



Scheme 1

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dichloromethane at 25 °C.

Copolymer A, D, and G. $^1\text{H NMR}$ (CDCl_3) δ 8.18-8.15 (2H, m, Ph), 7.50-7.25 (3H, m, Ph), 5.29 (1H, bs, OH), 5.28 (2H, bs, CH_2), 3.60 (5H, bs, $\text{CH}+\text{OCH}_3$), 1.90-1.73 (2H, bd, CH_2), 1.46 (18H, bs, *tert*-Bu), 1.30-0.85 (3H, bm, CH_3); IR (CDCl_3 , cm^{-1}) 3524 (OH, m), 2957 (*tert*-Bu, m), 1716 (CO, vs).

Copolymer B, E, and H. $^1\text{H NMR}$ (CDCl_3) δ 7.48 (2H, bs, Ph), 7.22-7.15 (4H, bm, Ph), 5.30 (1H, bs, OH), 5.12 (2H, bs, CH_2), 3.65 (5H, bs, $\text{CH}+\text{OCH}_3$), 1.88-1.65 (2H, bm, CH_2), 1.45 (18H, s, *tert*-Bu), 1.25-0.84 (3H, bm, CH_3); IR (CDCl_3 , cm^{-1}) 3627 (OH, m), 3335 (NH, m), 2958 (*tert*-Bu, m), 1713 (CO, vs).

Copolymer C, F, and I. $^1\text{H NMR}$ (CDCl_3) 7.25-7.11 (4H, bm, Ph), 7.06 (2H, s, Ph), 5.14 (1H, bs, OH), 3.66 (5H, bs, $\text{CH}+\text{OCH}_3$), 2.99 (2H, bt, CH_2), 2.86 (2H, bt, CH_2), 1.90-1.64 (2H, bm, CH_2), 1.44 (18H, s, *tert*-Bu), 1.25-0.85 (3H, bm, CH_3); IR (CDCl_3 , cm^{-1}) 3630 (OH, m), 2957 (t-butyl, m), 1718 (CO, vs).

Thermal Oxidation and Solvent Extraction. The polyethylene (PE) films were prepared by using compression molder at 170 °C and 2,000 psi for 5 min. Thermal oxidation of films was carried out in an ageing oven at 120 °C in air for 5 days and monitored with FT IR spectroscopy using the integral ratio of the peak of 1720/2025 cm^{-1} , the peak 2025 cm^{-1} chosen from the PE as a reference and the peak 1720 cm^{-1} generated from the oxidation of PE, to assess the extent of oxidation of polymers.⁶ The films were prepared by blending the monomers 1-3 or copolymers A-I with PE. Extraction of films with water was achieved in Soxhlet apparatus for 150 hours and monitored with FT IR spectroscopy using the peak height ratio of the carbonyl group of monomers or copolymers to the peak of 2025 cm^{-1} of PE.

Results and Discussion

Synthesis of Monomeric Antioxidants. Monomeric antioxidants **1-3** having maleimide group were prepared according to our previous method (Figure 1).⁵ These monomeric antioxidants bearing maleimide group could be used for higher MW antioxidants by polymerization.

Copolymerization of Monomeric Antioxidants 1-3. Monomeric antioxidants **1-3** were copolymerized with MMA by AIBN to obtain the desired polymers **A-I** (Scheme 1). Polymerization reactions were performed in THF solution at 60 °C. The polymerization results are summarized in Table 1. Proton NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the required polymer structures. Hindered phenolic antioxidants may interfere with the radical initiator because they are free radical scavengers to form a stable phenoxide radical, which is a source of antioxidation. Munteanu and his co-workers,⁴ however, reported that the hindered phenolic antioxidants could be homopolymerized even in the presence of free radical initiators. Recently we also confirmed that monomeric antioxidant **1** was grafted onto polyethylene by melt processing with a free-radical initiator such as dicumyl peroxide (DCP).⁷ It is known that hindered phenolic antioxidants trap the peroxy radicals (ROO^\cdot) rather than the alkyl radicals (R^\cdot) in the polymer stabilization mechanism.^{4d} Thus, our monomeric antioxidants **1-3** were, as expected, copolymerized in the presence of free-radicals. The copolymers were soluble in dichloromethane and THF. The intrinsic viscosity, measured in dichloromethane at 25 °C was in the range of 0.38-1.21 dL/g. The thermal behaviour of the copolymers was investigated by TGA to determine the thermal stability. The resulting polymers showed the thermal

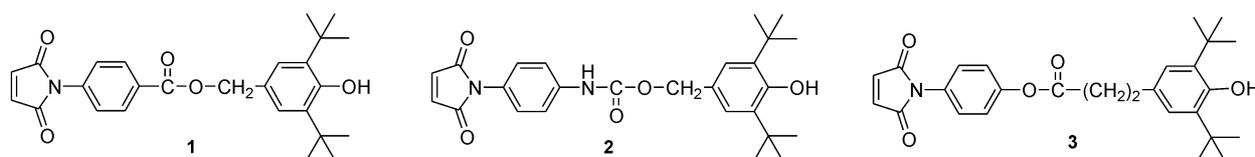


Figure 1. Prepared Antioxidants.

Table 1. Free Radical Copolymerization of **1**, **2**, and **3** with MMA in THF

Entry	Monomer	Monomer/MMA	Polymer	Yields (%)	Monomer (n)/MMA (m) ^a	M_w ($\times 10^5$) ^b	M_w/M_n	η_{int} (dL/g) ^b
1	1	1:5	A	>99	1:5	2.13	2.36	1.21
2	2	1:5	B	90	1:6	4.17	5.82	0.45
3	3	1:5	C	>99	1:5	0.69	1.86	0.57
4	1	1:10	D	>99	1:10	0.38	2.34	0.46
5	2	1:10	E	>99	1:10	2.77	3.09	0.41
6	3	1:10	F	>99	1:10	0.96	2.13	0.63
7	1	1:20	G	>99	1:20	1.52	1.96	0.44
8	2	1:20	H	75	1:18	0.95	2.05	0.38
9	3	1:20	I	>99	1:20	1.38	2.04	0.89

^aDetermined by $^1\text{H NMR}$ spectroscopy. ^bMeasured by GPC in THF with polystyrene standards. ^cIntrinsic viscosity of polymers determined in dichloromethane at 25 °C.

Table 2. Thermal Stability of Monomers 1-3 and Copolymers D-I

Antioxidant		1	2	3	D	E	F	G	H	I
Degradation	0%	175	200	275	240	229	278	242	200	282
temperature (°C) ^a	20%	229	228	348	355	351	347	362	344	360
	50%	347	262	378	391	393	376	393	391	387

^aCorresponding temperature of mass loss in TGA curves.

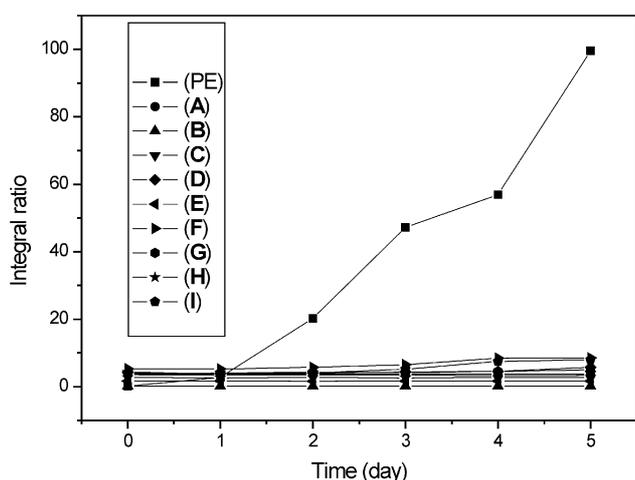


Figure 2. Antioxidative effect of the pure PE and blended films with 1 wt % copolymer A-I. Integral ratio ($1720\text{ cm}^{-1}/2020\text{ cm}^{-1}$) means the ratio of carbonyl peak generated from oxidation of PE to one of PE peaks as a reference in IR spectrum.

stability in the range of 200–282 °C, onset temperature of mass loss, as shown in Table 2. We shifted our attentions to examine the thermal antioxidative effect by the aging test and the resistance to extraction by water in the PE matrix. The change in peak integral ratio of $1720/2025\text{ cm}^{-1}$ versus aging time is shown in Figure 2. The carbonyl content of unstabilized PE drastically increased, while the PE films blended with 1 wt% copolymer antioxidant showed no increase of $1720/2025\text{ cm}^{-1}$ ratios for 5 days. These preliminary results indicate that the prepared copolymers have the antioxidative effect.⁶

In Soxhlet extraction with water, the films blended with monomers 1-3 were extracted showing that the height of carbonyl peak of monomers was diminishing in Figure 3, while the films containing copolymers were not almost lost in water extraction.

In summary polymeric antioxidants was successfully prepared by the copolymerization of monomeric maleimide 1-3 with MMA. The copolymers possess some stabilizing effect against thermal oxidation with oven aging in air at 120 °C for 5 days and also have the some resistance to water extraction.

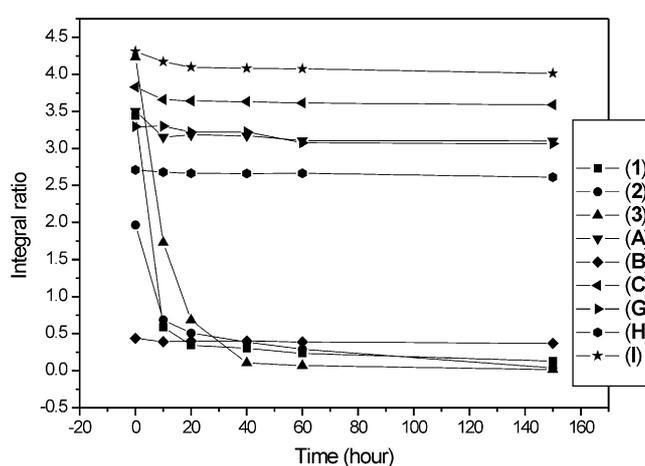


Figure 3. Extraction resistance of the PE blended films with monomers 1-3 and copolymers A-I. Integral ratio ($1720\text{ cm}^{-1}/2020\text{ cm}^{-1}$) means the ratio of carbonyl peak of antioxidants to one of PE peaks as a reference in IR spectrum.

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