The Inhibition of the Thermal Oxidative Degradation of Polypropylene by Various Phenanthrols

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Synopsis

All isomers of phenanthrol, 1-, 2-, 3-, 4-, and 9-phenanthrol, were prepared and the inhibitory effect of these compounds on the thermal oxidative degradation of isotactic polypropylene was examined by conventional oxygen uptake. The phenanthrols were found to be much more effective antioxidants than commercial 2,6-di-*tert*-butyl-4-methylphenol (abbreviated as BHT), and phenanthrene itself hardly showed any inhibitive effect. The effect of the phenanthrols was largely dependent on the position of the hydroxy group; the order of the effect was as follows: 1- > 4- > 2- > 3- > 9-phenanthrol > BHT. The phenanthrols were also good inhibitors of the radical polymerization of methyl methacrylate, and a fairly good correlation was observed between oxygen uptake and radical polymerization data.

INTRODUCTION

Recently, naturally degradable polymers or photo-degradable polymers have attained importance because of the pollution problem created by waste plastics.[1] These polymers, however, should be used in extremely limited fields because disposable polymers mean that valuable natural resources are used only once, and there is no distinct guarantee at present of the safety from secondary pollution.

On the other hand, the preparation of polymeric materials with good weatherability and the inhibition of commercial polymers to degradation still seem to be extremely important in the industrial fields. Thus, a series of studies on the inhibition of the degradation of polymeric materials has been continued. This paper deals with the inhibition of the thermal oxidative degradation of isotactic polypropylene by various phenanthrols.

EXPERIMENTAL

Preparation of Phenanthrols

1- and 4-Phenanthrol. In accordance with literature methods,[2] naphtalene was reacted with succinic anhydride in nitrobenzene in the presence of aluminum chloride, and the products (a mixture of two isomers) were separated by recrystallization using acetic acid. One of the isomers, β-(2-naphthoyl)propionic acid thus obtained was reduced to γ-(2-naphthyl)-

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butyric acid by the Clemmensen reduction, cyclized to 4-oxo-1,2,3,4-tetra-hydrophenanthrene under dehydration, and then dehydrogenated[3] to 4-phenanthrol on Pd-carbon.   1-Phenanthrol[4] was prepared from β-(1-naphthoyl) propionic acid in an analogous way.

2-, 3-, and 9-Phenanthrol[5].   The sulfonation of phenanthrene at 60°C for three days yielded a mixture of 1-, 2-, 3-, and 9-phenanthrenesulfonic acid. All sulfonic acids except the 1-acid were isolated, and alkaline fusion of each sulfonic acid at 300°C yielded the corresponding phenanthrols.

Thermal Oxidative Degradation

The isotactic polypropylene used was neat powder, finer than 100 mesh; crystallinity, 60%; intrinsic viscosity, 1.3; ash, 0.005–0.01%; additive, without any stabilizers (the same sample as used in a previous work[6]).   In a mortar, 100 parts of polymer were carefully mixed with 0.05, 0.1, 0.25, and 0.5 parts of each of the phenanthrols.   2,6-Di-*tert*-butyl-4-methylphenol and phenanthrene were also used as controls.

TABLE I
Melting Points of Additives and Oxygen Uptake Data at 130°C (t_{10} values)

Additive	Melting point, °C	t_{10}, min	
		0.5 phr[a]	0.05 phr
Phenanthrene	101	138	62
		147	58
		av. 143	60
1-Phenanthrol	156	24520	13760
		24940	13840
		av. 24730	13800
2-Phenanthrol	168	—	1300
			1372
			av. 1336
3-Phenanthrol	123	—	4410
			4380
			av. 4395
4-Phenanthrol	113.5	—	8700
			8810
			av. 8755
9-Phenanthrol	153	—	1630
			1625
			av. 1628
BHT[b]	68	2950	2410
		3050	2398
		av. 3000	2404
PP only	—	50	
		54	
		av. 52	

[a] Part per hundred resin.
[b] 2,6-Di-*tert*-butyl-4-methyl phenol.

The thermal oxidation was carried out using 100-mg samples under atmospheric pressure at 130°C and 150°C with a conventional oxygen absorption apparatus. Double determinations were made for each sample, and the effect of each phenanthrol was estimated by the oxygen uptake curve, reading the time required to absorb 10 ml oxygen per 1 g sample (t_{10}).

Polymerization of Methyl Methacrylate

In order to examine the inhibitory effect of the phenanthrol on the radical polymerization of methyl methacrylate (to estimate the induction period), the polymerization of methyl methacrylate was carried out in benzene solution at 50°C under the following conditions: concentration of monomer, 4.5 moles/l., benzoyl peroxide, 1×10^{-3} mole/l., and phenanthrol, 1×10^{-3} mole/l.

RESULTS AND DISCUSSION

The melting points of the additives and oxygen uptake data at 130°C (t_{10}) are shown in Table I. As shown in the table, some phenanthrols were found to be much more effective inhibitors for the thermal oxidation of polypropylene than a commercial antioxidant, 2,5-di-*tert*-butyl-4-methyl-phenol. Thus, the subsequent experiments were carried out at 150°C.

Typical oxygen uptake curves observed for isotactic polypropylene containing 0.5 parts per hundred resin (phr) of various phenanthrols at 150°C
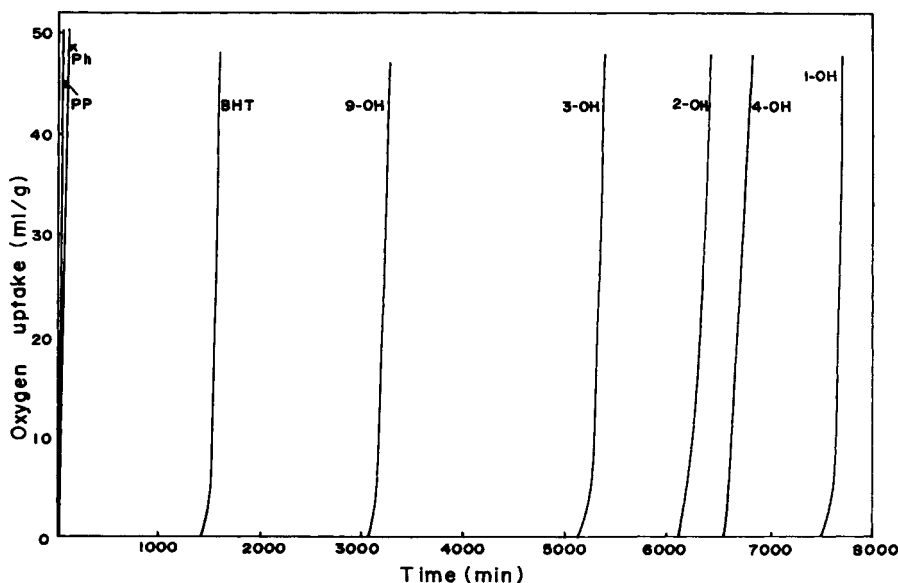

Fig. 1. Oxygen uptake curves at 150°C (containing 0.5 phr additive). PP: Poly-propylene only; BHT: 2,6-di-*tert*-butyl-4-methyl phenol; Ph: phenanthrene; 1-OH: 1-phenanthrol; 2-OH: 2-phenanthrol; 3-OH; 3-phenanthrol; 4-OH: 4-phenanthrol; 9-OH: 9-phenanthrol.

are shown in Figure 1. From the oxygen uptake curves observed for each samples (Table II), the t_{10} values were estimated, and the results are plotted against the amount of the additives, and shown in Figure 2.

The results apparently show that the phenanthrols are more effective antioxidants than the commercial antioxidant 2,6-di-*tert*-butyl-4-methyl-phenol, while phenanthrene itself hardly has any inhibitory effect on the oxidation of polypropylene.

TABLE II
Original Oxygen Uptake Data at 150°C (t_{10} values) for Figure 2

Additive	t_{10}, min			
	0.5 phr[a]	0.25 phr	0.1 phr	0.05 phr
Phenanthrene	23	21	20	20
	26	20	19	19
	av. 25	21	20	20
1-Phenanthrol	7689	5960	2810	2010
	7529	5908	2770	2075
	av. 7609	5934	2790	2043
2-Phenanthrol	6348	4753	195	165
	6059	4946	207	157
	av. 6204	4850	201	161
3-Phenanthrol	5463	4487	2140	432
	5445	4443	2180	426
	av. 5454	4465	2160	429
4-Phenanthrol	6610	5400	2907	1180
	6595	5442	2945	1036
	av. 6603	5421	2926	1108
9-Phenanthrol	3100	1324	1006	520
	3146	1330	1044	563
	av. 3123	1327	1025	542
BHT[b]	1434	1268	1020	570
	1553	1200	996	606
	av. 1484	1234	1008	588
PP only		20		
		19		
		av. 20		

[a] Part per hundred resin.
[b] 2,6-Di-*tert*-butyl-4-methyl phenol.

Obviously, the inhibitive effect depended on the concentration of the phenanthrols and increased with increasing amount of the additive. However, the nature of the dependence differed from one phananthrol to another. At phenanthrol concentrations higher than 0.25 phr, the effective order is as follows:
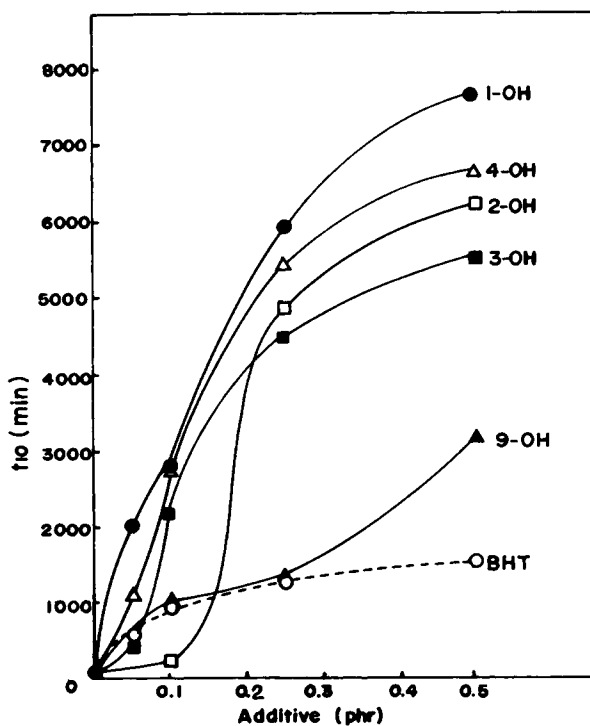
1- > 4- > 2- > 3- > 9-phenanthrol > BHT
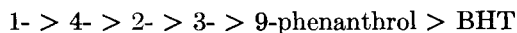
Fig. 2. Dependence of oxygen uptake (t_{10} value) at 150°C on the amount of additive
Symbols as in Fig. 1.

Davies and co-workers[7] determined the relative efficiency of various phenols including phenanthrol during the oxidation of tetralin, and demonstrated that antioxidant efficiency in the case of polycyclic phenols is roughly related to the energy of the most loosely held mobile electron in the compound in question. The antioxidant efficiency of the phenanthrols during the oxidation of isotactic polypropylene is fairly similar to that of oxidation of tetralin.

In general, α-naphthol is much more effective than β-naphthol.[7,8] This is dependent on the greater resonance stability of the α-naphthoxy than β-naphthoxy radical. In phenanthrene, it is widely acceptable that the 1- and 4-positions correspond to the α-position of naphthalene, and the 2- and 3-positions to the β-position.[9] It is, therefore, rational that 1-phenanthrol and 4-phenanthrol are more effective inhibitors than 2- and 3-phenanthrol. The 9-position of phenanthrene could be compared to either the α- or the β-position of naphthalene. However, the inhibitory effect of 9-phenanthrol is lower than that of any other phenanthrol. One of the reasons could be ascribed to the fact that the 9-phenanthrol is easily oxidized to phenanthrenequinone.

If the phenanthrols act as a radical scavengers in the oxidation of polypropylene, they also should inhibit the conventional radical polymerization

of vinyl monomers. To confirm the assumption, the inhibitory effect of various phenanthrols on the radical polymerization of methyl methacrylate initiated by benzoyl peroxide was examined, and the results were compared with the oxidation data (t_{10}) mentioned above.

In Figure 3, the induction periods in the radical polymerization were plotted against t_{10} values. As shown in the figure, 1- and 4-phenanthrols also show a large inhibitory effect on the radical polymerization of methyl methacrylate, and the induction period of the radical polymerization is relatively correlated with the oxidation data. Tne results apparently
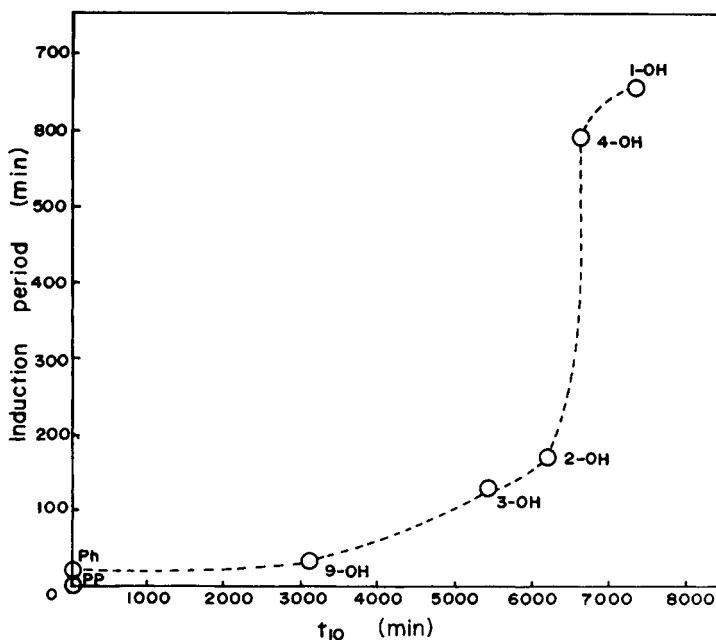

Fig. 3. Oxygen uptake (t_{10} value) at 150°C vs. induction period in radical polymerization. Symbols as in Fig. 1.

indicate that the phenanthrols act as radical scavengers both in the oxidation of polymers and polymerization of methyl methacrylate, and the inhibitory effect is largely affected by the position of the hydroxy group in the phenanthrols.

The phenanthrols can be prepared from phenanthrene by simple synthetic reactions, e.g., sulfonation and successive alkaline fusion, and the isomer mixture thus obtained could be sufficient for practical purposes. Phenanthrene itself is a major unused substance of coal tar at present. Therefore, the phenanthrols can be supplied at a reasonably low cost, and can be used as commercial antioxidants.

On the basis of the results obtained, the work of searching for more effective phenanthrene derivatives is being continued.

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