Effect of Various Triazine Derivatives on the Thermal Oxidative Degradation of Isotactic Polypropylene

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Synopsis

A number of triazine derivatives, mostly aryloxy-s-triazines, were prepared, and the effects of these compounds on the thermal oxidative degradation of isotactic polypropylene were examined by conventional oxygen uptake. Almost all triazine derivatives prepared showed a more or less inhibitive effect on the degradation of the polymer. Among them, α- and β-napthyloxy-s-triazines were found to be excellent inhibitors. On the basis of the results obtained, the relationship between inhibitive effect and the structure of the triazine derivatives is discussed.

INTRODUCTION

We have been studying the effect of various additives, including metallic compounds, on the thermal oxidative degradation of polymeric materials and exploring new antioxidants for conventional polymeric materials.[1-7] One of the authors (K. M.) has extensively studied the reactions of various triazine derivatives.[8-21] Thus, for a tentative new application of the derivatives, mostly aryloxy-s-triazines (partly aryl-s-triazines), the effect of the derivatives on the thermal oxidative degradation of isotactic polypropylene was examined, and naphthyloxy-s-triazines were found to be the most excellent inhibitors among the derivatives examined.

EXPERIMENTAL

Preparation of Triazine Derivatives

2-Chloro-4,6-disubstituted s-triazines were treated with corresponding phenols or naphthols in chloroform in the presence of sodium hydroxide at 60°C for 10 hr. After the chloroform layer was washed with aqueous sodium hydroxide solution (2–3%) and water, the solution was dried and evaporated and the residue was collected. The crystalline products were recrystallized from suitable solvents. Several products thus obtained were photoirradiated in ethanol solution using a low-pressure mercury lamp. Thus, the corresponding hydroxyphenyl-s-triazine derivatives were pre-

pared by the photorearrangement of aryloxy-s-triazines.   Typical prep-
arations were as follows.

2,4-Dimethoxy-6-phenoxy-s-triazine.   Into a mixture of 60 ml methyl
alcohol and 20.2 g sodium bicarbonate, 18.5 g cyanic chloride was added
and stirred at ca. 35°C for 7 hr.   The reaction mixture was then poured
into 300 ml ice water, and the crystalline precipitate (2-chloro-4,6-
dimethoxy-s-triazine) was filtered, dried, and recrystallized from ligroin
(mp 76–77°C).   Into a solution of 26 g 2-chloro-4,6-dimethoxy-s-triazine
thus obtained in 300 ml chloroform, a solution of 17 g phenol in 100 ml 8%
aqueous sodium hydroxide solution was added dropwise with stirring at
room temperature and was stirred at 60°C for 8 hr.   The chloroform layer
was then washed with sodium hydroxide and removed under reduced pres-
sure, and the crystalline products obtained were recrystallized from ligroin
(yield 92%).

2,4-Dimethoxy-6-β-naphthyloxy-s-triazine.   Into a solution of 48 g
β-naphthol in 200 ml 7% aqueous sodium hydroxide, a solution of 53 g
2-chloro-4,6-dimethoxy-s-triazine in 300 ml chloroform was added drop-
wise with stirring at room temperature and was stirred at 60°C for 10 hr.
The chloroform layer was washed with sodium hydroxide (2–3%) and dried
with calcium chloride, then chloroform was removed under reduced pres-
sure, and the products were recrystallized from benzene (yield quantita-
tive).

Thermal Oxidative Degradation

The isotactic polypropylene used was neat powder, finer than 100 mesh
(the same sample as used in a previous work[7]).   In a mortar 100 parts of
polymer was carefully mixed with 0.5 part of the triazine derivatives pre-
pared, and the thermal oxidation was carried out using 100-mg samples
under atmospheric pressure at 120°C with a conventional oxygen absorp-
tion apparatus prepared in our laboratory.   Double determinations were
made for each sample, and the effect of each derivative was estimated by
the oxygen uptake curve reading the time required to absorb 10 ml of
oxygen per 1 g sample (t_{10}).

RESULTS AND DISCUSSION

Typical oxygen uptake curves observed for isotactic polypropylene con-
taining various triazine derivatives at 120°C are shown in Figure 1 (for
2,4-dimethoxy-6-aryloxy-s-triazines) and Figure 2 (for 2,4-dimethoxy-6-
aryl-s-triazines and 2,4-dimethoxy-6-naphthyloxy-s-triazines).

From oxygen uptake curves observed for each sample, the time required
to absorb 10 ml oxygen per 1 g sample was estimated (t_{10}), and results are
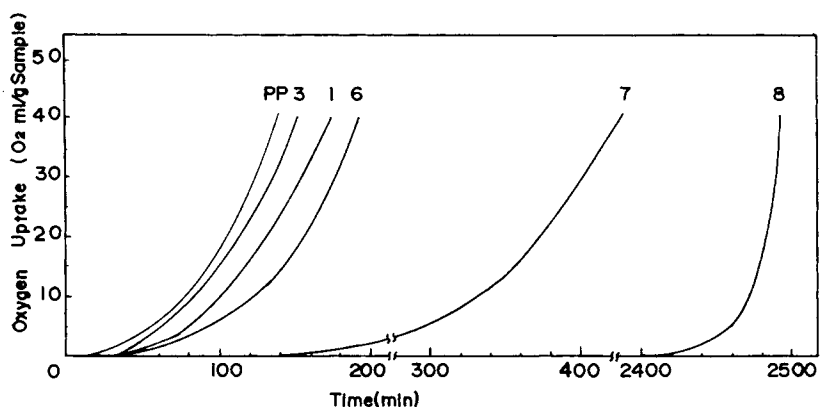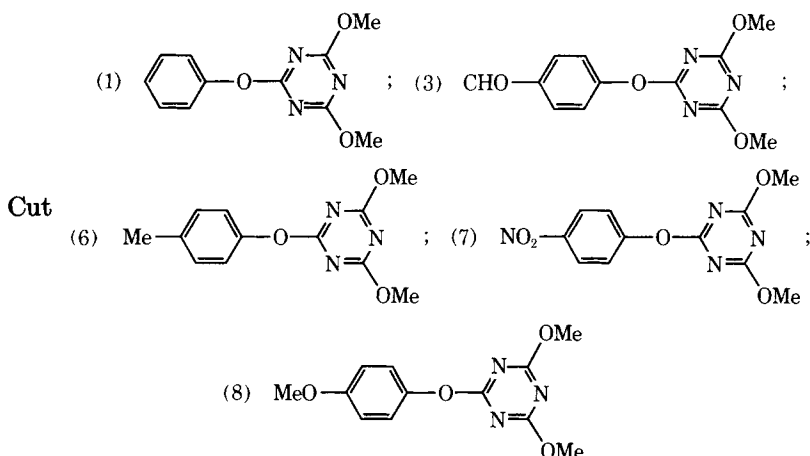summarized in Tables I and II.   The original oxygen absorption data are
shown in Table III.

Fig. 1. Oxygen uptake curves for isotatic polypropylene containing triazine derivatives, at 120°C: (PP) pure polypropylene only:
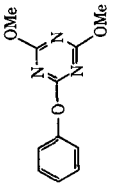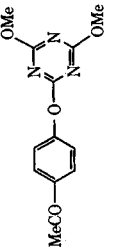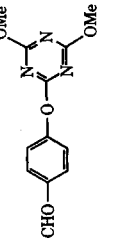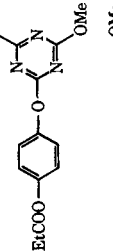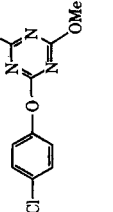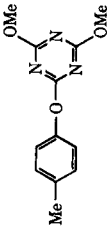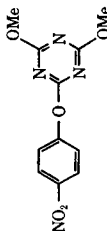

From Figures 1 and 2 and Tables I and II, one might observe that almost all triazine derivatives examined have a more or less inhibitive effect for the thermal oxidative degradation of polymer.

In the case of para-substituted 2-aryloxy-4,6-dimethoxy-s-triazines (Compounds 1–9), the compounds containing an electron-withdrawing group on the para position of the aryloxy ring showed 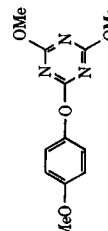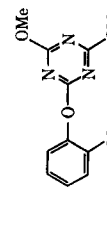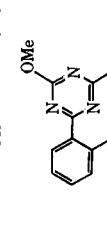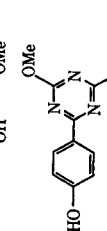much less inhibitive effect, except for compound 7 (NO_2 substituent). However, the compounds containing an electron-donating group (6, 8, and 9), particularly in the presence of a methoxyl group (8), was fairly effective.

In the case of hydroxyaryl derivatives prepared from the corresponding aryloxy-s-triazine derivatives by photorearrangement, no pronounced inhibitive effect was observed for the inhibition of the thermal degradation of polymers, but disubstituted derivatives (12, 13, and 14) showed slightly better effect than monosubstituted derivatives (10 and 11). Both β- and α-naphthyloxy derivatives (15 and 16) showed an excellent inhibitive effect, but the latter was much more effective than the former.
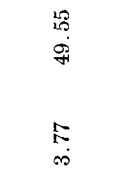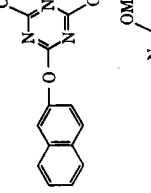
TABLE I

Data of 2,4-Dimethoxy-s-triazines (6-Aryloxy, -Aryl, and -Naphthyloxy)

No.	Structure	Melting point, °C	Elemental analysis				Recrystn. solvent	O_2 uptake t_{10}, min
			Calcd, %		Found, %			
			C	H	C	H		
Pure PP		—	—	—	—	—	—	79
1[a]		102–102.5	56.65	4.75	56.55	5.01	ligroin	109
2		119–120	56.72	4.76	56.78	4.62	benzene	84
3		146–147	55.17	4.24	55.59	4.29	benzene	86
4		121.5–123	55.08	4.97	54.91	5.00	benzene	107
5[a]		86–87.5	49.36	3.77	49.50	3.96	ligroin	108

No.	Structure	m.p. (°C)	Calcd. C	Calcd. H	Found C	Found H	Solvent	
6[a]	(OMe, OMe; Me-phenyl-O-triazine)	89–90.5	58.29	5.30	57.83	5.06	ligroin	132
7[b]	(OMe, OMe; NO_2-phenyl-O-triazine)	136–136.5	47.48	3.62	47.81	3.78	ligroin	340
8[a]	(OMe, OMe; MeO-phenyl-O-triazine)	80–81	54.75	4.98	54.51	5.09	ligroin	2475
9	(OMe, OMe; Me-phenyl-O-triazine)	87.5–88.5	58.29	5.30	58.72	5.39	ligroin	132
10[a]	(OMe, OMe; OH-phenyl-triazine)	112–113	56.65	4.75	57.08	5.01	ligroin	109
11[a]	(OMe, OMe; HO-phenyl-triazine)	238–239	56.65	4.75	56.46	5.14	acetone–water	117

(continued)

TABLE I (continued)

| No. | Structure | Melting point, °C | Elemental analysis | | | | Recrystn. solvent | O_2 uptake t_{40}, min |
| | | | Calcd, % | | Found % | | | |
			C	H	C	H		
12[a]		145–146	49.36	3.77	49.55	3.78	ligroin	199
13[a]		132–133	58.29	5.30	58.68	5.57	ligroin	130
14[a]		134–135	54.75	4.98	54.49	5.12	ligroin	437
15		117–118	63.60	4.63	63.52	4.47	benzene	7180
16		87.5–88.5	63.60	4.63	62.98	4.78	benzene	25100

[a] Partly reported in the literature.[16]
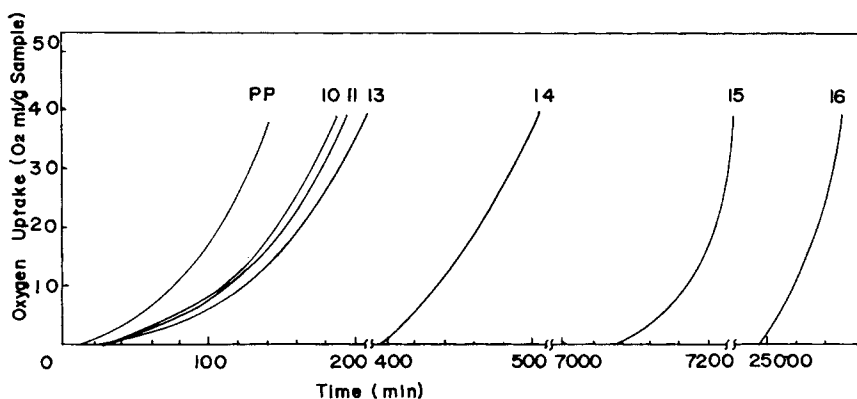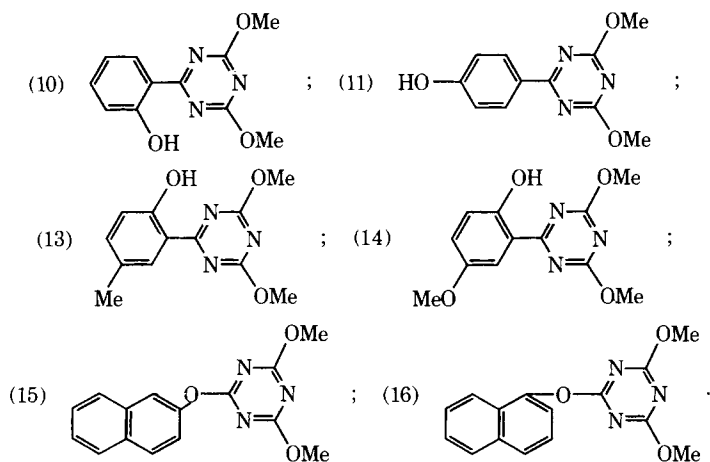[b] Partly reported in the literature.[9]

Fig. 2. Oxygen uptake curves for isotatic polypropylene containing triazine derivatives, at 120°C: (PP) pure polypropylene only:
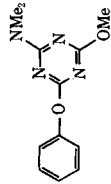

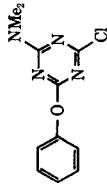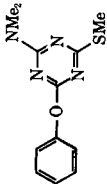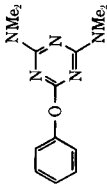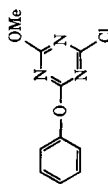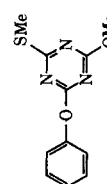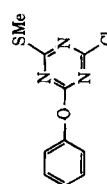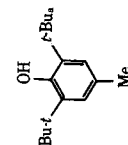In the case of 2,4-disubstituted 6-phenoxy-s-triazine derivatives (Table II), no remarkable effect was observable. However, compounds 21 and 22 (2-phenylamine-substituted derivatives) and 26 (2-dimethylamine-4-methylthio-disubstituted derivative) were failrly effective in inhibiting the thermal oxidation of the polymer.

As mentioned above, the inhibitive effect of the aryloxy and hydroxy-aryl-s-triazine derivatives is not sufficient for them to be practical anti-oxidants of the conventional polymeric materials, and to give an adequate explanation for the role of the triazine derivatives examined is rather difficult at present. However, it may be roughly said that the inhibitive effect of the triazine derivatives with an electron-withdrawing group in the aryloxy ring was less than that of the derivatives with an electron-donating group, with the exception of compound 7 (NO_2 group). If the assumption is true, the triazine derivative seems to exhibit the inhibitive effect by homolytic cleavage of the —O—C— (attached to triazine ring) bond giving phenoxy or aryloxy radical.

TABLE II
Data of 2,4-Disubstituted 6-Phenoxy-s-triazines

No.	Structure	Melting point, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Recrystn. solvent	O_2 uptake t_{10}, min
17		225–226	55.04	4.62	54.24	3.68	benzene	105
18		231–232	48.55	3.17	49.05	2.87	methanol	110
19		132.5–134	58.53	5.73	57.88	5.32	benzene–ligroin	122
20		147–149	50.75	3.83	50.25	3.85	methanol–water	96
21		140.5–141.5	65.30	4.79	64.97	4.51	benzene–ligroin	794
22		102–104	60.31	3.71	60.41	4.22	benzene–ligroin	310
23		136.5–137	57.13	5.66	56.70	5.54	methanol–water	158

No.	Structure (substituents)	mp (°C)	Found %		Calcd %		Solvent	
24	triazine: NMe$_2$, OMe, O-phenyl	94–95	60.46	5.46	59.83	6.01	ligroin	134
25	triazine: NMe$_2$, Cl, O-phenyl	139.5–140.5	52.66	4.42	52.41	4.29	ligroin	90
26	triazine: NMe$_2$, SMe, O-phenyl	66–67	54.94	5.37	55.65	5.65	ligroin	351
27	triazine: NMe$_2$, NMe$_2$, O-phenyl	106–107	60.22	6.60	60.59	6.54	ligroin	152
28	triazine: OMe, Cl, O-phenyl	128–129	50.54	3.49	50.21	3.37	ligroin	102
29	triazine: SMe, OMe, SMe, O-phenyl	112–114	53.21	4.47	54.89	4.36	ligroin	115
30	triazine: SMe, Cl, O-phenyl	80.5–82.5	47.34	3.18	48.34	3.16	ligroin	155
	OH, Bu-t, t-Bu, Me (phenol)	70	81.82	10.91	—	—	—	7150

a 2,6-Di-*tert*-butyl-4-methylphenol (commercial phenolic antioxidant) (Product of Tokyo Kasei Ltd. Co.)

TABLE III
The Original Oxygen Absorption Data

No.	Exp. 1	Exp. 2	Ave.
Pure PP	80	78	79
1	108	110	109
2	82	86	84
3	85	87	86
4	110	104	107
5	106	109	108
6	132	132	132
7	325	355	340
8	2410	2540	2475
9	130	134	132
10	107	110	109
11	120	114	117
12	190	207	199
13	130	130	130
14	450	424	437
15	7260	7100	7180
16	25300	24900	25100
17	100	110	105
18	116	104	110
19	120	124	122
20	100	92	96
21	800	787	794
22	300	320	310
23	147	168	158
24	130	138	134
25	91	88	90
26	340	361	351
27	143	161	152
28	98	103	102
29	111	119	115
30	160	150	155
[a]	7050	7250	7150

[a] 2,6-Di-*tert*-butyl-4-methylphenol.

Thus, the stability of the radical formed should play an important role. Apparently, the stability of the aryloxy radical is fairly consistent with the inhibitive effect for low molecular weight hydrocarbons.[22] However, since in the case of 6-phenoxy-2,4-disubstituted *s*-triazine derivatives, the inhibitive effect was affected by the substituents in the triazine ring, one must take into consideration the triazine fragment radical produced. In the case of hydroxyaryl-*s*-triazine derivatives, abstraction of hydrogen from the hydroxyl group may be important. In the case of naphthyloxy-*s*-triazine derivatives, which showed an excellent effect, if naphthyloxy radical is formed by the cleavage of the —O—C— (attached to triazine ring) bond, the stability of the α-naphthyloxy radical must be assumed to be much higher than that of β-naphthyloxy radical. The result mentioned above is consistent with the stability of the naphthyloxy radical.[22,23]

Since all triazine derivatives examined are colorless crystalline substances, they are of great advantage as additives for the polymeric materials. Also, as mentioned above, a few triazine derivatives newly prepared were found to be excellent inhibitors for the thermal oxidative degradation of isotactic polypropylene.

Although no adequate explanation can be given for the inhibitive mechanism at present, it is quite likely that an aryloxy radical formed by the cleavage of —O—C— (attached to triazine ring) bond is the most important factor. On the basis of their tentative assumption, we are examining details of the inhibitive mechanism of the triazine derivatives and are preparing new and more effective triazine derivatives.

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