Thermal Properties of Higher Molecular Weight Light Stabilizers of the Benzophenone Type

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Synopsis

The thermal properties of some new higher molecular weight UV absorbers of the 2-hydroxybenzophenone type have been studied using DTA andTG methods, and the obtained results have been compared with the thermal properties of 2-hydroxy-4-*n*-octyloxybenzophenone. The DTA, TG, and DTG curves and initial and maximum rate temperatures are given. The maximum rates of active decomposition and residues were also evaluated.

INTRODUCTION

It is necessary to know the thermal properties of light stabilizers which are added to polymers to meet the requirements of processing, mainly for fiber-forming polymers. At high processing temperatures, the stabilizers evaporate from polymer, and thus their concentration and efficiency in the polymer substrate decrease. The contamination of the technological equipment is a very important factor, since it causes technical difficulties in spinning as well as a deterioration of the environment for service personnel.

The DTA and TG methods are most advantageous for the investigation of thermal properties. These may be studied with the stabilizers themselves, or in mixtures with usable polymer.[1,2] Of course, more valuable results for industrial application are obtained by carrying out the measurements in the polymer system; but in such a case, the thermograms obtained are much more complicated. However, they reflect the properties of the polymer applied. In some cases, the properties of the polymers may overlap the thermal properties of the stabilizers. In addition, the nature of the thermograms is affected by the treatment and the geometry of the samples, since in polymer systems parallel reactions with contradictory effects take place.[3] For instance, in samples with large external and internal surfaces, an exothermic oxidation (which can result in increase in weight) predominates. In the case of thick samples with a small surface, where there are no suitable conditions for diffusion of oxygen, endothermic reactions resulting in a weight loss prevail.

In the present paper, we are concerned with the thermal properties of photostabilizers investigated by thermoanalytical methods.
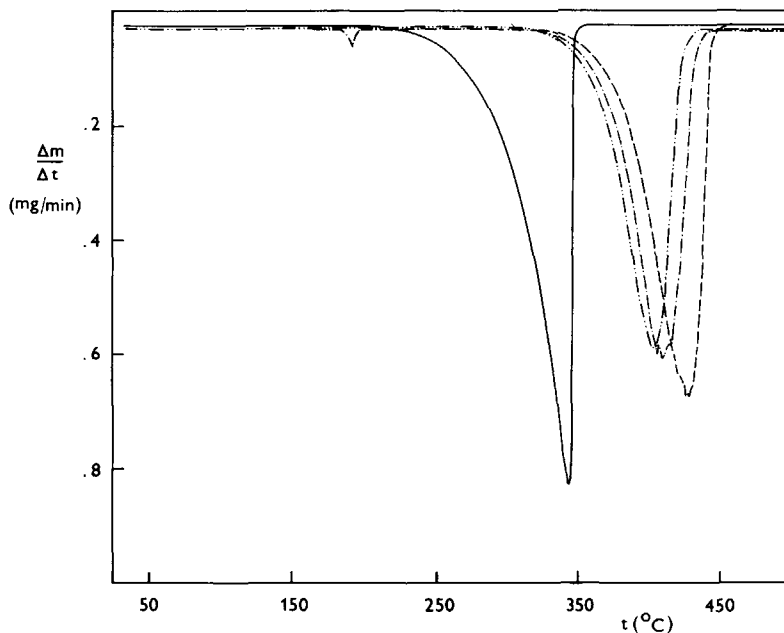
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Fig. 1. DTG curves of samples S (—), OT (– · · –), T (– · –), and 2T (- - -).

EXPERIMENTAL

Samples OT, T, and 2T were prepared according to reference 4, A and AT according to reference 5, and 16T and 33T according to reference 6. The substances were purified either by crystallization or precipitation and dried to constant weight in a vacuum oven. The commercial UV absorber 2-hydroxy-4-n-octyloxybenzophenone (S) was used as a standard.

Thermal properties of stabilizers were measured on a Thermoanalyser 2 (Mettler) apparatus. A nitrogen flow of 7 l./hr, a heating rate of 4°/min, sample weights of 7 mg, Pt–Rh–Pt thermocouples, and Al_2O_3 as standard were used for the DTA.

RESULTS AND DISCUSSION

The UV absorbers of the 2-hydroxybenzophenone type used can be divided according to their nature into substances of the polyester polymer types of general formula
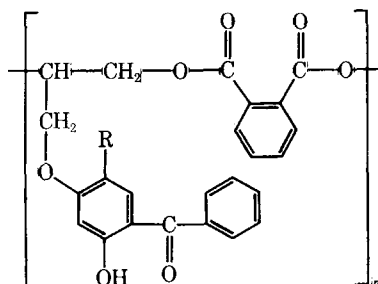
TABLE I
Thermal Properties of Higher Molecular Weight UV Absorbers

Stabilizer	Mol weight[a]	mp, °C		t_i, ±10 °C[b]	t_{max}, ±2 °C[c]	v_{max}, mg/min[d]	R_{330}, %[e]	R_{450}, %[f]	E, kcal/mole[g]
		Kofler	DTA						
S	(326)		51	200	346	0.80	40	0	22.0[h]
OT	489 (485)	147–8	152	315	404	0.56	98	20	47.2
T	(541)	187–9	192	320	408	0.57	95	11	45.6
2T	586 (597)	199–201	206	325	431	0.64	98.5	2.5	41.8
A	1800	—	—	260	360	0.50	88.5	14	38.7
AT	2300	—	—	275	358	0.70	91	14	51.3
33T	1670 (1450)	—	—	310	426	0.65	93	18	49.6
16T	1920 (2390)	—	—	310	429	0.57	95	20	32.8

a Molecular weights determined by VPO (Knauer) in benzene at 37°C; the values in parentheses are calculated molecular weights.
b The initial temperature of weight loss.
c The temperature of maximum rate of active decomposition.
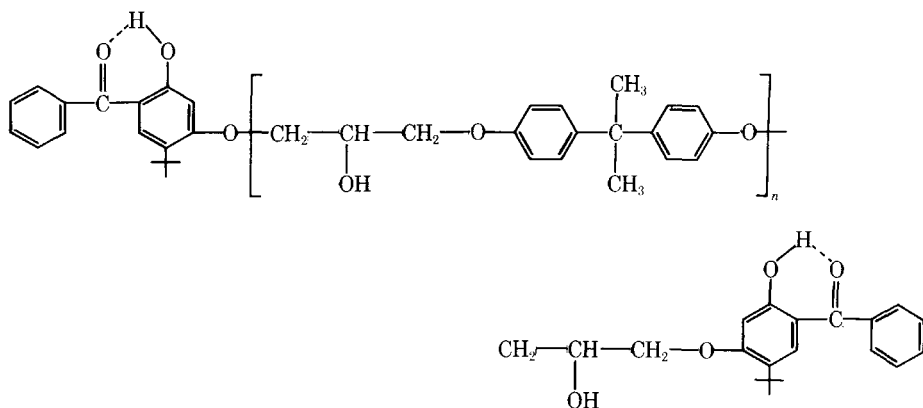d The maximum rate of active decomposition.
e Residue at 330°C.
f Residue at 450°C.
g The activation energy of active decomposition.
h 27.6 kcal/mole in lit.[7]

where R is hydrogen (sample A) or *tert*-butyl (sample AT), the addition products of epoxy resins with 2,4-dihydroxy-5-*tert*-butylbenzophenone (33T and 16T according to molecular weight of epoxy resin) of general formula

and the group of double benzophenones of general formula
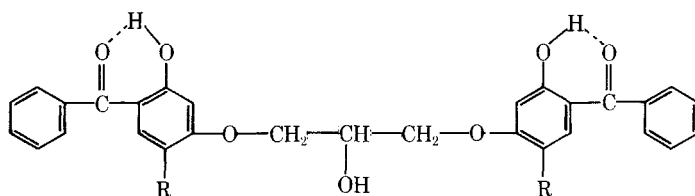
where R stands for hydrogen (OT), or one (T) or two *tert*-butyl groups (2T). In the last group of substances, the effect of *tert*-butyl substitution manifests itself already in the melting points of crystalline benzophenones and increases with the number of substituents from ca. 150° to 200°C, as given in Table I. It is remarkable that the introduction of the first substituent has a particular influ-
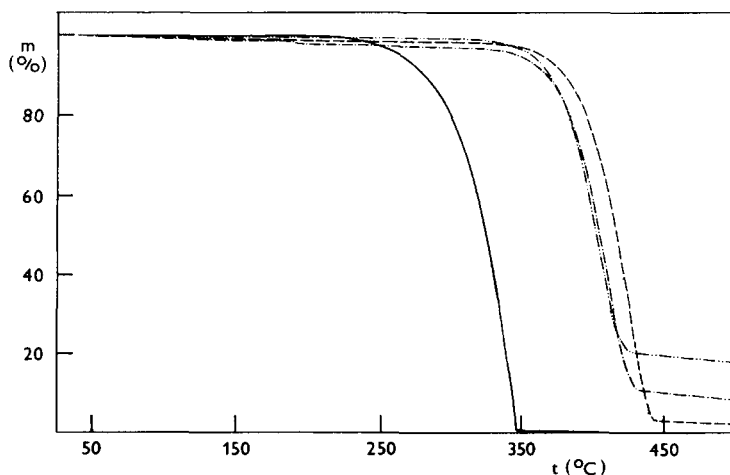

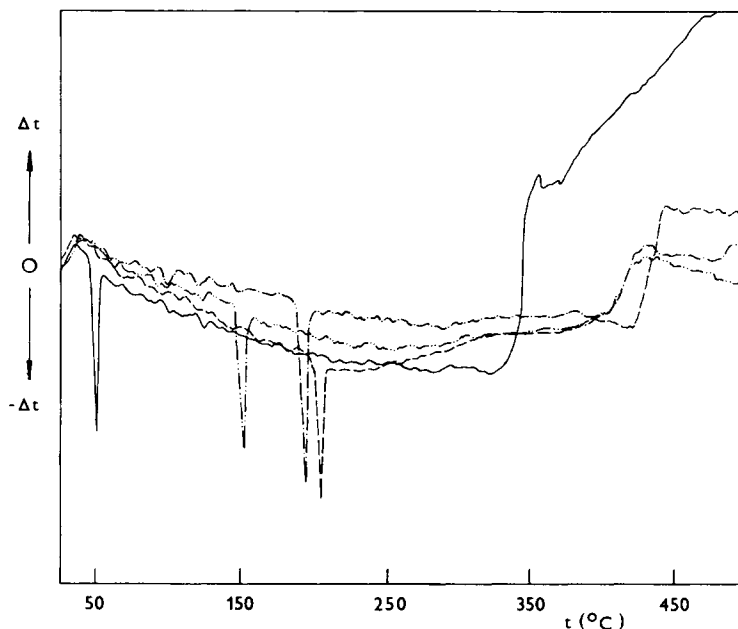Fig. 2. TG curves of samples S, OT, T, and 2T (denoted as in Fig. 1).

Fig. 3. DTA curves of samples S, OT, T, and 2T (denoted as in Fig. 1).

ence. The effect of substituent will be markedly reflected also on the volatility and thermal stability of these compounds. The higher thermal stability caused by increasing number of substituents may be estimated according to the initial decomposition temperature t_i, or better, according to the temperature at which the rate of decomposition is maximum, t_{max} (from 404° to 430°C).
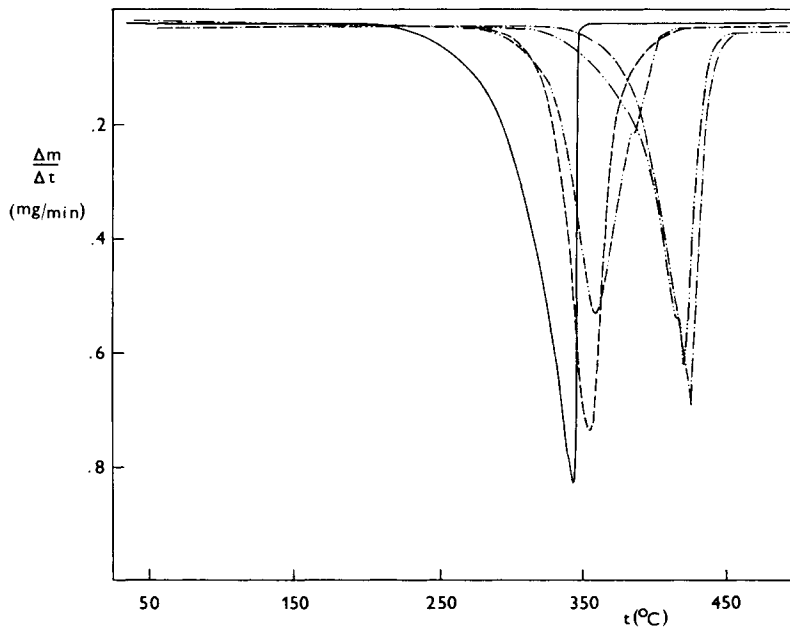

Fig. 4. DTG curves of samples S (—), A (– – – $\cdot$ – – –), AT (- -), 33T (– $\cdot$ –), and 16T (– $\cdot$ $\cdot$ –).
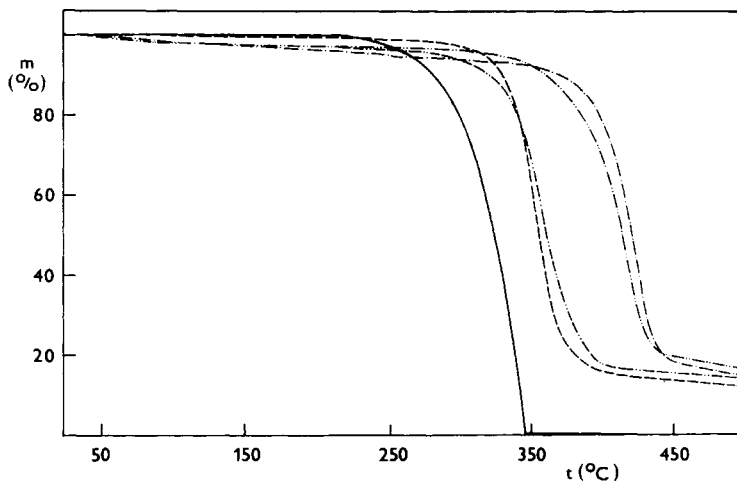
Fig. 5. TG curves of samples S, A, AT, 33T, and 16T (denoted as in Fig. 4).

In contrast to the melting points, the introduction of the second *tert*-butyl group into a molecule exerts more marked influence on t_{max}. The presence of *tert*-butyl groups does not only affect t_{max}, but also the maximum rate of active decomposition, v_{max}, which increases with the content of *tert*-butyl substituents.

Figure 1 shows a comparison between the DTG thermograms of the stabilizers and the commercially produced effective stabilizer S. It is important that stabilizer S is considerably volatile according to the TG result (Fig. 2). At a temperature of 330°C which is used in the processing of polymers (e.g., spinning of polypropylene), only a 40% residue remains after the TG analysis performed under the conditions described. At 350°C, compound S completely evaporates. Samples OT, T, and 2T differ substantially from the commercial stabilizer. At minimum, a 95% residue is preserved at 330°C. The DTG curves (Fig. 1) and TG curves (Fig. 2) are of different character. The thermal decomposition occurs at temperatures above 350°C, and there remains some residue, which is highest with the unsubstituted OT sample.

Figure 3 shows the DTA results of the compounds discussed. One can see sharp endothermic peaks corresponding to melting points as well as an exothermic domain which is probably due to secondary reactions of the evaporating or decomposing stabilizers.

The next figures (Figs. 4, 5, and 6) give thermograms of commercial sample S, synthetized polyester stabilizers (A, AT), and stabilizers of the epoxide type (16T, 33T). Both types of polymer stabilizers are thermally more stable than sample S, and it can be roughly stated that the polyester stabilizers show a temperature of active decomposition which is higher at least by 50°C, and the epoxide stabilizers show a temperature of active decomposition which is higher at least by 100°C than that of the commercial sample. The lower stability of polyesters is caused by a lower resistance of the ester bond to thermal destruction. In spite of this, the decomposition of both polyesters proceeds at a lower rate than in the case of stabilizer S; and for unsubstituted polyester A, v_{max} is lower than
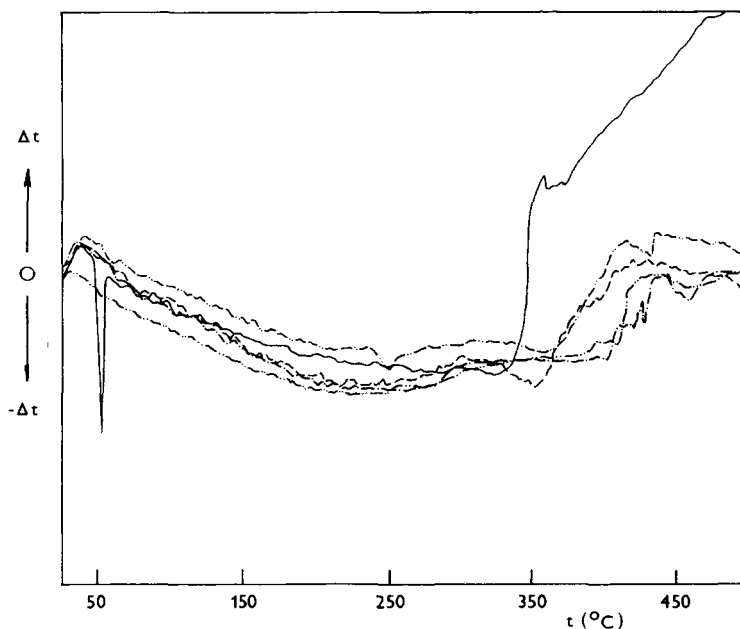
Fig. 6. DTA curves of samples S, A, AT, 33T, and 16T (denoted as in Fig. 4).

for the substituted AT sample. As to stabilizers of the epoxide type, the sample with greater molecular weight (16T) has a lower rate of decomposition than sample 33T. For both samples, v_{max} is lower than that of stabilizer S. For the decomposition of polymer stabilizers, the calculated activation energies were considerably higher than for the decomposition of the commercial stabilizer (Table I). The residue at 450°C was ca. 15–20%.

On the DTA thermograms of the polymer stabilizers, no pronounced effects which would correspond to melting points or endothermic decomposition were observed. At temperatures above 350°C, a weak exothermic region was observed.

CONCLUSIONS

Thermal properties of the commercial and some new types of light stabilizers were investigated by the methods of thermal analysis (TG, DTG, and DTA). On the basis of the thermograms, it can be concluded that the commercial stabilizer is not sufficiently thermally stable for industrial demands and evaporates at the temperatures which are usually used in the processing of polypropylene. The doubling of two benzophenone molecules yields a product with much different properties, and the replacement of hydrogens in the 5-position of the aromatic type by *tert*-butyl groups enhances the stability.

The polymeric types of stabilizers exhibit a higher thermal stability which is sufficient for application. From the point of view of thermal properties, the epoxide type appeared to be more convenient as compared with polyesters.

The determination of the thermal properties of the polymer systems containing the mentioned stabilizers will be the subject of further studies.

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