Temperature Limit of Inhibition of Thermo- oxidative Degradation of Polystyrene and Poly(methyl methacrylate) by Antioxidants

B. B. Troitskii[a]; L. S. Troitskaya[a]; A. S. Yakhnov[a]; A. A. Dmitriev[a]; L. I. Anikina[a]; V. N. Denisova[a]; M. A. Novikova[a]

[a] Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny, Novgorod, Russia

PLEASE SCROLL DOWN FOR ARTICLE

Temperature Limit of Inhibition of Thermo-oxidative Degradation of Polystyrene and Poly(methyl methacrylate) by Antioxidants

B. B. TROITSKII*, L. S. TROITSKAYA, A. S. YAKHNOV, A. A. DMITRIEV, L. I. ANIKINA, V. N. DENISOVA and M. A. NOVIKOVA

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina 49, Nizhny Novgorod 603600, Russia

Investigation has been made on the influence of aromatic and sterically hindered amines, sterically hindered phenols, S- and P-containing compounds on the thermo-oxidative degradation of PS and PMMA by a DSC method under oxygen. The oxidative degradation of antioxidants themselves has been studied under the identical conditions. The dependences of the temperature of the onset of degradation of the polymers on antioxidant concentrations have been obtained. It has been shown that the upper temperature limit of inhibition of the thermo-oxidative degradation of PS and PMMA by well-known effective antioxidants is in the range 280–295°C and depends insignificantly on the chemical structure of polymer. The suggestion was made that the value of the temperature limit of inhibition depends to a great extent on intensive oxidative decomposition of antioxidant itself.

Keywords: Polystyrene; poly(methyl methacrylate); thermo-oxidative degradation; antioxidants

1. INTRODUCTION

It is well known [1–3] that aromatic and sterically hindered amines, sterically hindered phenols, S- and P-containing compounds are

---

*Corresponding author.

315

widely used as antioxidants for polymeric materials. It is very important to know temperature limit of effective inhibition of the thermo-oxidative degradation of different polymers by various stabilizers. Investigation has been made on the influence of great number of antioxidants (phenols, amines, S- and P-containing compounds) on the thermo-oxidative aging of polyethylene and polypropylene using oxygen absorption technique [2, 4]. It has been shown that at temperatures of about 280–290°C all stabilizers investigated do not effectively retard oxidation of these polymers [2, 4]. Some compounds are not effective antioxidants at more low temperatures [2, 4]. The upper temperature limit of inhibition of the thermo-oxidative degradation of polyethylene and polypropylene by stabilizers (280–290°C) does not depend on mechanism of their retardation influence [2, 4].

This study deals with the determination of temperature limit of inhibition of the thermo-oxidative aging of polystyrene (PS) and poly(methyl methacrylate) (PMMA) by aromatic and sterically hindered amines, sterically hindered phenols, S- and P-containing compounds.

Many tests have been proposed for evaluating stabilizers [5]. In recent years thermal analysis methods such as differential analysis and differential scanning calorimetry (DSC) are applied in the study of the thermal and thermo-oxidative degradation and stabilization of polymers. It is the ability of these methods to detect the thermal consequences of the onset of degradation which makes them useful techniques for polymers showing exothermic or endothermic degradation. We have used a DSC method for studying the effect of antioxidants on the degradation of the polymers.
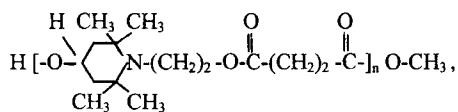
2. EXPERIMENTAL

2.1. Materials

PMMA and PS were prepared by bulk polymerization as described before [6].

The following stabilizers have been used:

Tinuvin 622 (Ciba-Geigy)

$$H[-O-\underset{\underset{CH_3\ CH_3}{|}}{\overset{\overset{H\ CH_3\ CH_3}{|}}{\bigcirc}}N-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-]_n\ O-CH_3,$$

Tinuvin 770 (Ciba-Geigy)

$$HN\underset{CH_3\ CH_3}{\overset{CH_3\ CH_3}{\bigcirc}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-\underset{CH_3\ CH_3}{\overset{CH_3\ CH_3}{\bigcirc}}NH,$$
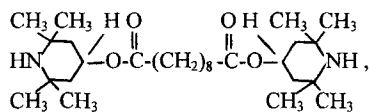
Chimassorb 944 (Ciba-Geigy)

$$\left[\,\cdots\,\right]_n,$$

Neozone D (Bayer), m.p. 108°C ⬡⬡—NH—⬡ ,

S-47, m.p. 145-146°C

⬡ - NH - ⬡ - O-CH₂ -CH(OH)-CH₂ -O - ⬡ - NH - ⬡ ,

S-49, m.p. 166-167°C

⬡⬡ - NH - ⬡ - O-CH₂ -CH(OH)-CH₂ -O - ⬡ - NH - ⬡⬡ ,
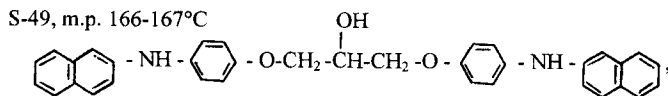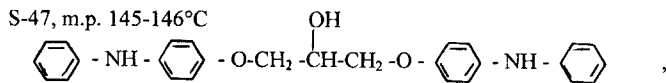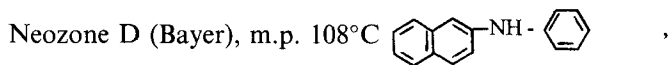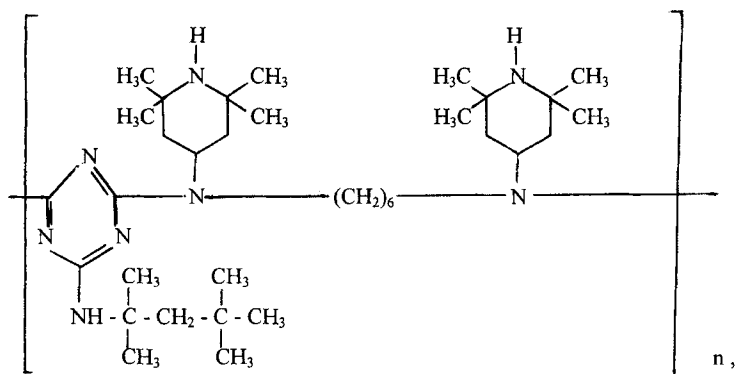
Phenozane-23, m.p. 80 – 85°C

$$(HO - \underset{}{\bigotimes} - CH_2 -CH_2 -\overset{O}{\overset{\|}{C}} -OCH_2)_4\, C \,,$$
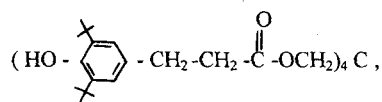
Phenozane-27, m.p. 139 – 140°C

$$(HO - \underset{}{\bigotimes} - CH_2 -CH_2 -\overset{O}{\overset{\|}{C}} -OCH_2 -)_2 \,,$$

Phenozane-30, m.p. 66°C
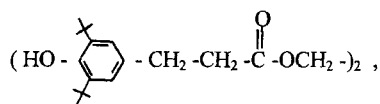
$$(HO - \underset{}{\bigotimes} - CH_2 -CH_2 -\overset{O}{\overset{\|}{C}} -OCH_2 -CH_2)\, S \,,$$
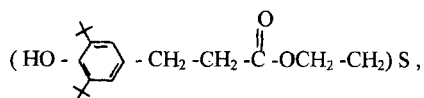
Si-phenol, m.p. 116 – 117°C

$$(HO - \underset{}{\bigotimes} - CH_2 -CH_2 -O)_4\, Si \,,$$
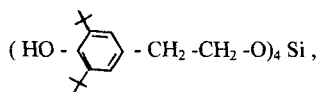
dilauryl thiodipropionate (DLTP),m.p. 39-40°C , $S(CH_2 -CH_2 -\overset{}{\underset{O}{\overset{\,}{C}}}-OC_{12}H_{25})_2$,

dinaphthyl thiodipropionate (DNTP),m.p. 70°C , $S(CH_2 -CH_2 -\underset{O}{\overset{}{C}}-O - \bigotimes)_2 ,$

tri(p-nonylphenyl) phosphite (Polygard, Naugatuck), $(C_9H_{19} - \bigcirc - O)_3\, P.$

     Phenols were prepared in the Institute of Chemical Physics of Russian Academy of Sciences.

2.2. Methods

The degradation of PS and PMMA films was carried out by a DSC method in dynamic oxygen (40 ml/min) at $100 - 500°C$ with scanning rate of $5°C/min$ and under isothermal heating conditions. A charge of $1.0 \times 10^{-6} - 3.0 \times 10^{-6}$ kg of PS or PMMA was used for each experiment. A DSC-7 Perkin-Elmer instrument was used.

Films of PS and PMMA without additives and with antioxidants were prepared as described previously [6].

The degradations of antioxidants were investigated by a DSC method in oxygen under dynamic heating conditions. A charge of 1.0×10^{-6} kg of compound was used for each experiment.

3. RESULTS AND DISCUSSION

DSC curves of the degradation of PS and PMMA in dynamic oxygen have been represented previously [6]. They have exotherms for polymer oxidation process. The DSC cuves show that the temperature of the onset of intensive degradation of polymer, T_0, is 220°C and 275°C for PS and PMMA, respectively. In the degradation of the polymers in an inert gas, no appreciable changes in baseline are seen in the DSC curves up to 368°C and 320°C for PS and PMMA, respectively. It follows that in the degradation of the polymers under oxygen, the onset of degradation at 220°C for PS and 275°C for PMMA is due to the branched chain nature of the oxidation reaction process.

An as example, in Figures 1–4 DSC curves of the PS thermo-oxidative degradation in the presence of some antioxidants, such as Tinuvin 770 (Fig. 1), S-49 (Fig. 2), Phenozane-30 (Fig. 3) and Si-phenol (Fig. 4) are represented. As can be seen from Figures 1–4, in the presence of antioxidants, the values of T_0 for PS are more than 220°C.

Figures 5–7 illustrate the dependences of T_0 on concentrations of aromatic and sterically hindered amines (Fig. 5), sterically hindered phenols (Fig. 6) and S- and P-containing compounds (Fig. 7) in PS thermo-oxidative degradation. It is seen that the chemical structure of antioxidants affects these dependences. Beginning with definite concentration of an additive, the maximum value of T_0, T_0^{max}, is observed (Figs. 5–7). The value of T_0^{max} changes slightly with further increase in an antioxidant concentration. The value of T_0^{max} is a temperature

B. B. TROITSKII *et al.*

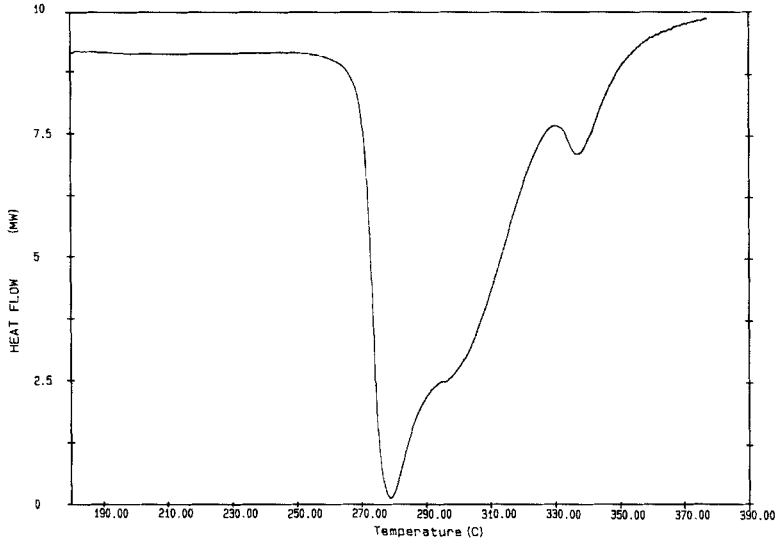FIGURE 1   DSC curve (oxygen, 5°C/min) for PS with addition of 9.8×10^{-4} mol/kg Tinuvin 770.
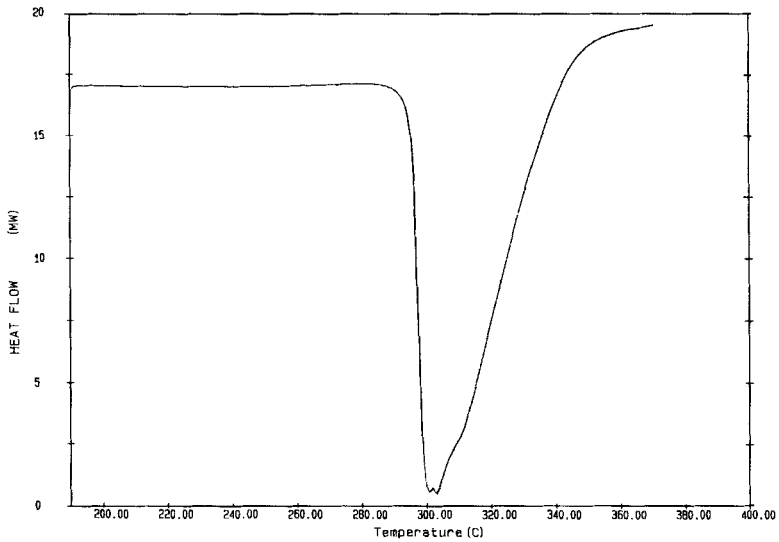

FIGURE 2   DSC curve (oxygen, 5°C/min) for PS with addition of 7.3×10^{-3} mol/kg S-49.
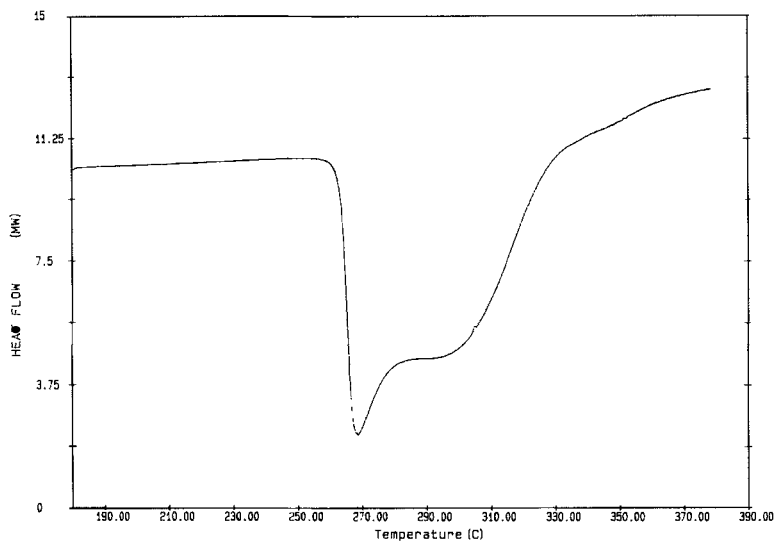
FIGURE 3   DSC curve (oxygen, 5°C/min) for PS with addition of 1.3×10^{-3} mol/kg Phenozane-30.
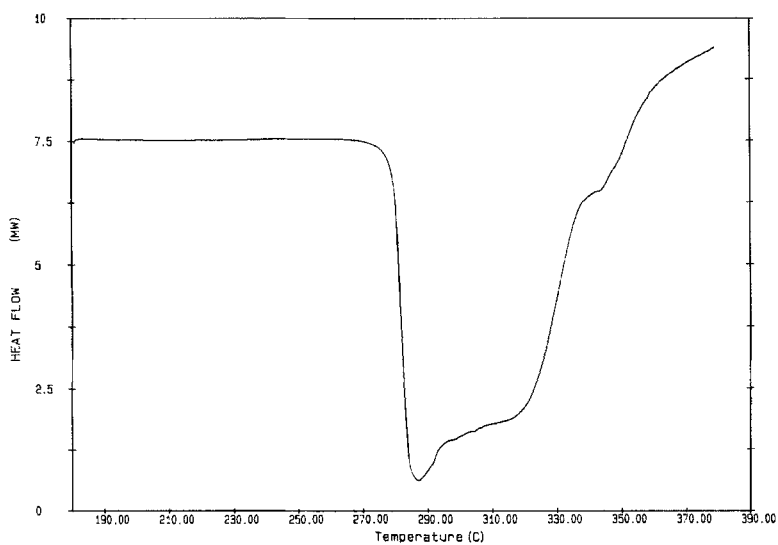
FIGURE 4   DSC curve (oxygen, 5°C/min) for PS with addition of 8.48×10^{-3} mol/kg Si-phenol.
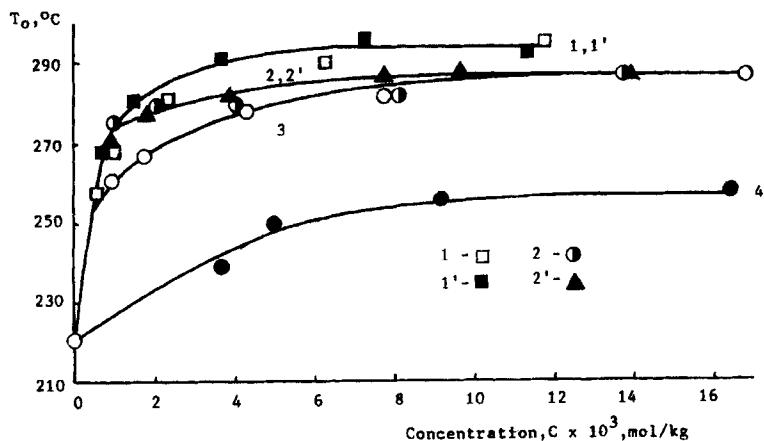
FIGURE 5   Dependences of T_0 on concentrations of amines in the thermo-oxidative degradation of PS under dynamic heating conditions. (1) S-47; (1 ') S-49; (2) Chimassorb 944; (2 ') Tinuvin 770; (3) Tinuvin 622; (4) Neozone D.

FIGURE 6   Dependences of T_0 on concentrations of phenols in the thermo-oxidative degradation of PS under dynamic heating conditions. (1) Phenozane-30; (1 ') Phenozane-27; (1 ") Phenozane-23; (2) Si-phenol.

limit of effective inhibition of the thermo-oxidative degradation of polymer by an antioxidant. The value of T_0^{max} depends on the chemical structure of the latter. The values of T_0^{max} are summarized in Table I.
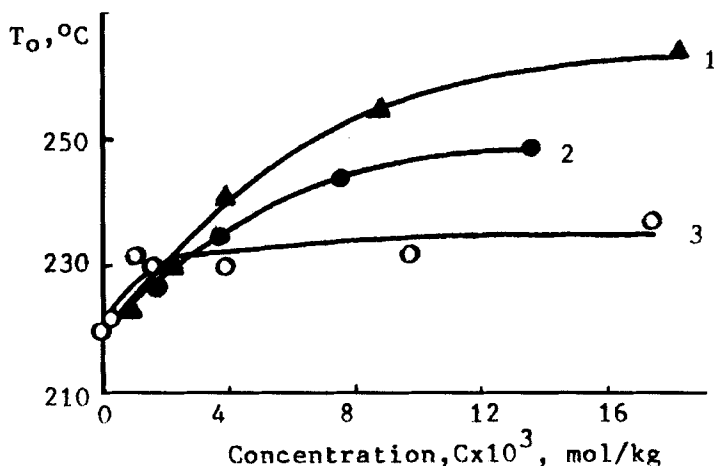
FIGURE 7 Dependences of T_0 on concentrations of S- and P-containing compounds in the thermo-oxidative degradation of PS under dynamic heating conditions. (1) DHTP; (2) DLTP; (3) Polygard.
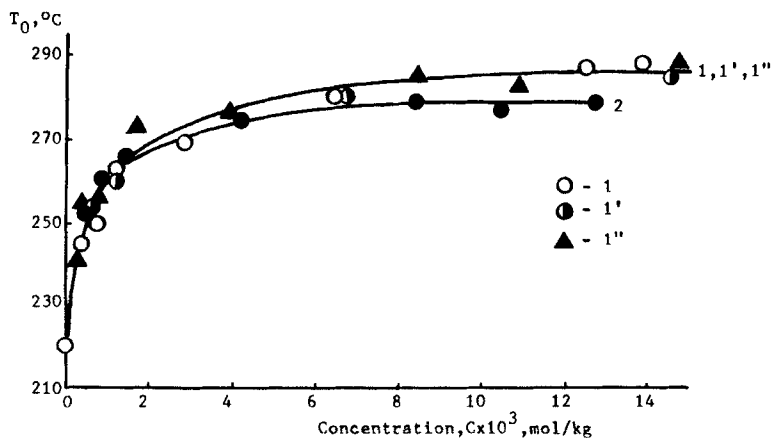
TABLE I The values of T_0^{max} in the thermo-oxidative degradation of PS and PMMA in the presence of antioxidants and the values of T_0^{stab} in the thermo-oxidative degradation of antioxidants themselves

Antioxidant	$T_0^{max}(^\circ C)$		$T_0^{stab}(^\circ C)$
	PS	PMMA	
Tinuvin 622	286		267
Tinuvin 770	286		210
Chimassorb 944	286	294	219
S-47	293		225
S-49	293		
Neozone D	256		247
Phenozane-23	286		
Phenozane-27	286		235
Phenozane-30	286		254
Si-phenol	279	285	230
DLTP	248		245
DHTP	263		
Polygard	235		239

Figure 5 shows that among amines investigated aromatic amines S-47 and S-49 are more effective antioxidants. In their presence, the value of T_0^{max} for PS is 293°C (Tab. I). Sterically hindered amines, Tinuvin 622, Tinuvin 770 and Chimassorb 944, have approximately the same

inhibition effectivenesses which are less than those of S-47 and S-49. In the presence of these amines, the value of T_0^{max} for PS is 286°C (Tab. I). In the presence of Neozone D, T_0^{max} is about 30°C less (Tab. I).

As can be seen from Figure 6, in the thermo-oxidative degradation of PS, inhibition efficiences of sterically hindered phenols investigated differ a little at small concentrations (up to about 2×10^{-3} mol/kg) but in their presence, the values of T_0^{max} are somewhat different (Tab. I). In the presence of Phenozane-23, Phenozane-27 and Phenozane-30, T_0^{max} is about 286°C. With addition of Si-phenol, T_0^{max} is slightly less (about 279°C).

Figure 7 illustrates that at small concentrations, S- and P-containing compounds studied have approximately the same efficiencies of retardation of the thermo-oxidative degradation of PS but in the presence of these antioxidants, the values of T_0^{max} for PS differ. In the presence of DNTP, T_0^{max} is 263°C and with addition of DLTP, T_0^{max} is less (about 250°C) (Tab. I). In the presence of Polygard, the value of T_0^{max} for PS is considerably less (about 235°C) (Tab. I).

The results obtained show that effectivenesses of inhibition of the thermo-oxidative degradation of PS at elevated temperatures ($>200°C$) by sterically hindered phenols and amines and some aromatic amines differ a little (Figs. 5 and 6 and Tab. I). S- and P-containing compounds investigated have considerably less inhibiting efficiencies (Figs. 5–7 and Tab. I). The temperature limit of inhibition of the thermo-oxidative degradation of PS by the effective antioxidants (amines and phenols) is in the range of 280°C to 295°C (Tab. I).

We studied the thermo-oxidative degradation of PS in the presence of Si-phenol by a DSC method under isothermal heating conditions at different temperatures. The concentrations of Si-phenol at which T_0 for PS is equal to T_0^{max}, where taken. Figure 8 represents the dependences of induction periods on temperature at two concentrations of Si-phenol. Exrapolation of the curves of these dependences on *absciss* axis shows that induction period is not observed at about 280°C. This temperature limit of inhibition of the thermo-oxidative degradation of PS by Si-phenol coincides with the value of T_0^{max} obtained in the degradation of the polymer under dynamic heating conditions (Tab. I).

The thermo-oxidative degradation of PMMA has been investigated in the presence of effective antioxidants, such as Chimassorb 944 and Si-phenol under dynamic heating conditions. Figure 9 represents the
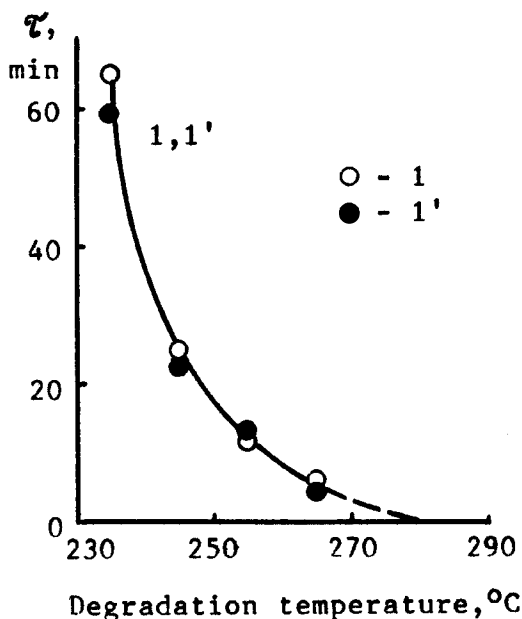
FIGURE 8   Dependences of induction period (τ) on degradation temperature in the thermo-oxidative degradation of PS under isothermal heating conditions in the presence of Si-phenol at different concentrations: (1) 8.5×10^{-3} mol/kg; (1') 12.8×10^{-3} mol/kg.

dependences of T_0 for PMMA on concentrations of these compounds. It is seen that in the presence of Si-phenol, T_0^{max} is about 285°C and with addition of Chimassorb 944, $T_0^{max} = 294$°C. These values of T_0^{max} for PMMA are reasonably close to those for PS (Tab. I).

It is well known [1] that in the thermo-oxidative degradation, PS is much less stable than PMMA due to the presence of fragments with hydrogen atoms near the tertiary carbon atoms which have less energy of C—H bonds than C—H bonds in PMMA. As mentioned above, the value of T_0 for PMMA is 55°C higher. It seems to be generally agreed that in the case of PS, initiation of the oxidative process is due to abstraction of hydrogen atoms near the tertiary carbon atoms [7, 8].

In the papers [7, 8] the thermo-oxidative aging of PS over a temperature range from 249°C to 300°C has been studied. It has been shown that water is the main volatile product. In the thermo-oxidative degradation of PS at elevated temperatures, the mechanism of oxidation of hydrocarbons in the liquid phase is believed to be operative [7, 8].
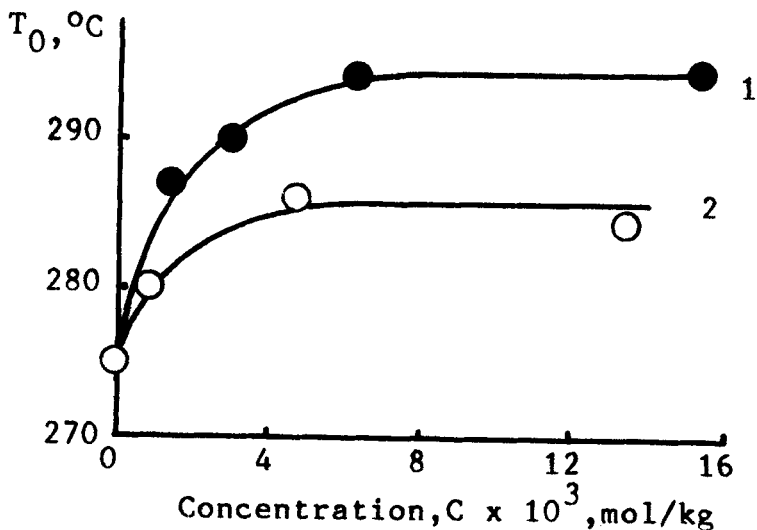
FIGURE 9 Dependences of T_0 on concentration of Chimassorb 944 (1) and Si-phenol (2) in the thermo-oxidative degradation of PMMA under dynamic heating conditions.

The thermo-oxidative degradation of PMMA has been investigated up to 320°C [9, 10]. It has been reported [9, 10] that at elevated temperatures (> 200°C), the major low molecular weight product of this process is methyl methacrylate ($> 90\%$) and the main reaction is the reaction of depropagation initiated owing to oxidation of the main chain. In PMMA thermo-oxidative degradation at elevated temperatures apart from the monomer, the following compounds are generated in significant amounts: 2-methyl-oxirane carbonic acid methyl ester, methyl pyruvate, dimethyl itaconate and acetaldehyde [9].

From the aforesaid, it appears that the thermo-oxidative stability and the thermo-oxidative degradation of PS differ considerably from those of PMMA. As mentioned above, in the thermo-oxidative degradation of these polymers in the presence of effective antioxidants, the values of T_0^{max} for PMMA are reasonably close to those for PS. The upper temperature limit of inhibition of the thermo-oxidative degradation of PS and PMMA by effective antioxidants is about 280–295°C (Tab. I). This upper temperature limit coincides practically with that of inhibition of the thermo-oxidative degradation of polyethylene and polypropylene by antioxidants (280–290°C) which was obtained using oxygen absorption technique [2, 4]. It may be concluded that chemical

structure of polymer has insignificant influence on the value of the upper temperature limit of inhibition of the thermo-oxidative degradation of polymers by well-known antioxidants.

We also studied the degradation of antioxidants themselves by the DSC method in oxygen under the dynamic heating conditions identical to those employed in the degradation of the polymers. The DSC curve for the degradation of Neozone D shows endotherm and exotherm which correspond to the volatility and to the oxidation, respectively. Above 210°C, Neozone D has great volatility. As mentioned above, at elevated temperatures, Neozone D is less effective antioxidant than other amines investigated (Fig. 5). One can assume that this may be connected with great volatility of Neozone D. The latter decreases the concentration of this antioxidant in polymer. The DSC curves demonstrate that other compounds studied do not considerably volatilize up to the onset of intensive oxidation of the antioxidants, T_0^{stab}. The DSC curves for some antioxidants are represented in Figures 10–13. These figures illustrate that no appreciable changes in baseline are seen in the DSC curves up to T_0^{stab}. The DSC curves for antioxidants show that exotherms which are attributed to the oxidation, have complicated outlines (Figs. 10–13). It may be assumed that this is
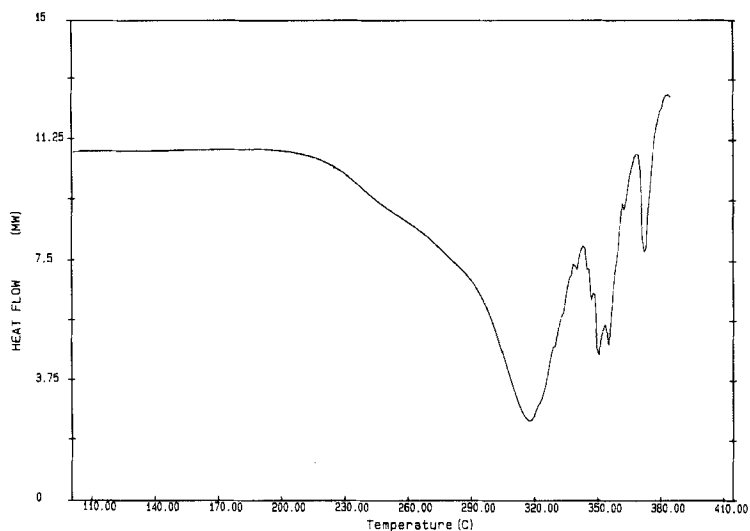

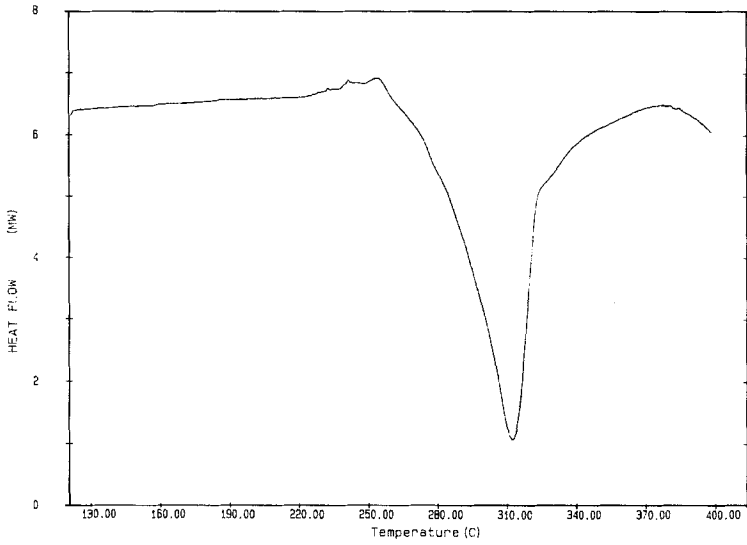FIGURE 10   DSC curve (oxygen, 5°C/min) for Chimassorb 944.

B. B. TROITSKII *et al.*

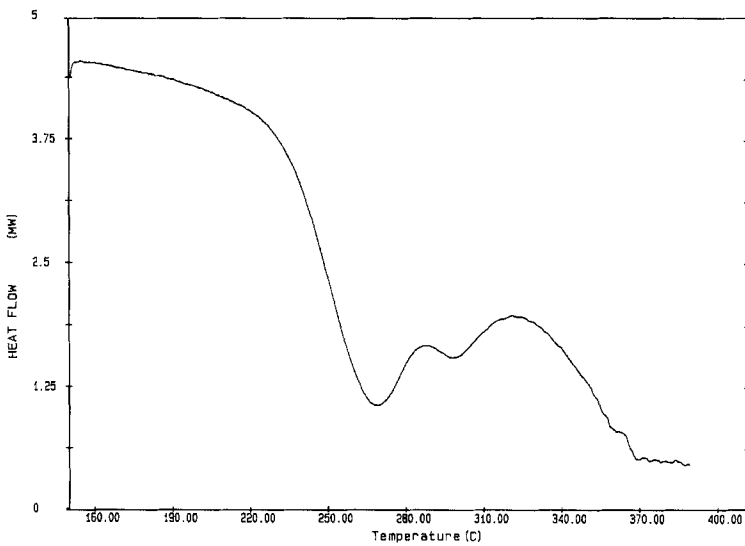FIGURE 11   DSC curve (oxygen, 5°C/min) for Phenozane-30.

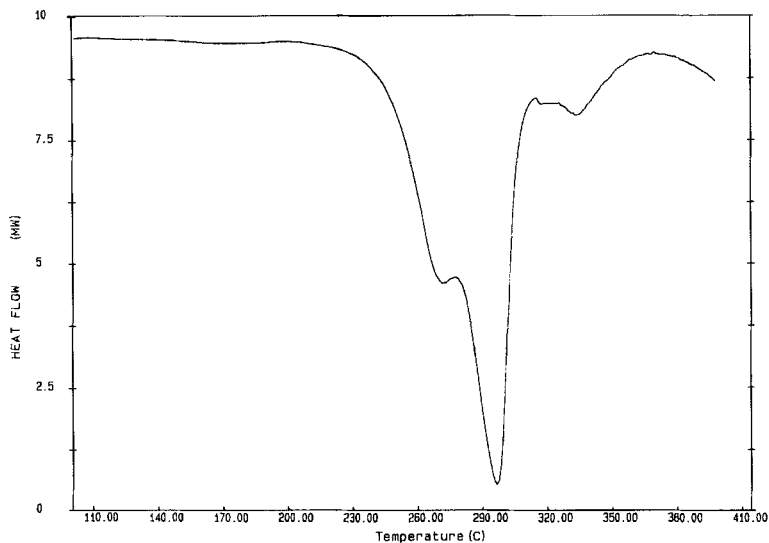FIGURE 12   DSC curve (oxygen, 5°C/min) for Si-phenol.

FIGURE 13 DSC curve (oxygen, 5°C/min) for DLTP.

connected with elimination of volatile products in the oxidative decomposition of antioxidants at temperatures above T_0^{stab}. Table I summarizes the values of T_0^{stab}. It is seen that in the case of sterically hindered phenols and amines and aromatic amine S-47, the values of T_0^{stab} are considerably less than the values of T_0^{max} for PS and PMMA in the thermo-oxidative degradation of the polymers in the presence of these antioxidants. It may be assumed that the values of T_0^{max} depend to a great extent on intensive oxidative decomposition of antioxidants themselves with elimination of volatiles which is observed at temperatures above T_0^{stab}. It is of interest to note that in the case of S- and P-containing compounds and Neozone D, the values of T_0^{max} agree closely with the values of T_0^{stab} (Tab. I).

4. CONCLUSION

In the present study the dependences of the temperature of the onset of the thermo-oxidative degradation of PS and PMMA on concentrations of aromatic and sterically been obtained. The temperature limits

of effective inhibition of the polymers by antioxidants have been determined.

Data obtained by the use of different techniques, such as oxygen absorption technique [2, 4] and the DSC method (present study) show that the upper temperature limit of inhibition of the thermo-oxidative degradation of polyethylene, polypropylene, PS and PMMA by well-known effective antioxidants is in the range from 280°C to 295°C and depends insignificantly on the chemical structure of polymer. The suggestion was made that the value of the temperature limit of inhibition of the thermo-oxidative degradation of polymers depends to a great extent on intensive oxidative decomposition of antioxidant itself.

Acknowledgements

References

[1] Grassie, N. and Scott, G. (1985). Polymer Degradation and Stabilization. Cambridge University Press, Cambridge.
[2] Shlyapnikov, Yu. A., Kiryushkin, S. G. and Mar', A. P. (1986). In: *Antioxidative Stabilization of Polymers*. Khimia, Moscow.
[3] Denisov, E. T. (1990). Oxidation and Destruction of Carbochain Polymers. Khimia, Leningrad.
[4] Edemskaya, V. V., Miller, V. B. and Shlyapnikov, Yu. A. (1974). *Vysokomol. Soedin.*, **B16**, 489.
[5] Billingham, N. C., Bott, D. C. and Manke, A. S. (1981). Developments in Polymer Degradation, Vol. 3, Ed. Grassie, N., *Applied Science*, London, p. 63.
[6] Troitskii, B. B., Troitskaya, L. S. and Yakhnov, A. S., *Europ. Polym. J.*, submitted.
[7] Jellinek, H. H. G. and Lipovac, S. N. (1970). *Macromolecules*, **3**, 231.
[8] Jellinek, H. H. G. and Lipovac, S. N. (1970). *Macromolecules*, **3**, 237.
[9] Song, J., Fischer, Ch.-H. and Schnabel, W. (1992). *Polym. Degrad. Stab.*, **36**, 261.
[10] Kopylova, N. A., Semchikov, Yu. D. and Terman, L. M. (1976). *Vysokomol. Soedin.*, **B18**, 198.