Effects of Thymolphthalein on Thermo-Oxidative Stability of High-Density Polyethylene in Melt and Solid States

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ABSTRACT: *The present work aimed to evaluate capability of a new molecular structure to stabilize polyethylene against thermal oxidation. Hence, effects of 3,3-bis(4-hydroxy-2-methyl-5-propane-2-ylphenyl)-2-benzofuran-1-one (thymolphthalein) on the thermo-oxidative stability of high-density polyethylene (HDPE) in both solid and melt states were investigated and compared with those of SONGNOX 1010, a commercially used phenolic antioxidant for the polymer. Oven aging experiments at 90 °C followed by Fourier Transform Infrared (FT-IR) spectroscopy showed that thymolphthalein at concentrations of 0.1-1.0 wt% improves thermo-oxidative stability of the polymer strongly in the solid state so that its stabilization efficiency is comparable to that of SONGNOX 1010. Furthermore, measurements of Oxidation Onset Temperature (OOT) and Oxidative Induction Time (OIT) of the polymer samples revealed that thymolphthalein modifies thermo-oxidative stability of the polymer in the melt state remarkably. So that, an increase in OOT value of the polymer as large as 36 °C was obtained by addition of 0.1 wt% of thymolphthalein. It was also confirmed that thymolphthalein does not interfere with the stabilization action of the phenolic antioxidant in the polymer neither in the melt or in the solid state. Finally, a mechanism for the stabilization action of thymolphthalein in the polymer was proposed.*

KEYWORDS: *Antioxidant; Oxidation; Polyethylene; Stabilization.*

INTRODUCTION

During the past decades, numerous research works have been devoted to studying thermo-oxidative degradation of polyethylene (PE) as well as stabilization of this commodity polymer against thermal oxidation [1-3]. Thermo-oxidative degradation of the polymer during high temperature melt processing as well as its solid state weathering proceed through a self-propagating free radical chain reaction (the so-called auto-oxidation) which alters molecular structure of the polymer through generation of different oxidation groups such as acids, ketones, esters and so on [4-6]. Formation of alkyl radical (P•) and alkyl peroxyl radical (POO•) are of key importance in this process [7]. However, the worst feature of the process is formation of hydroperoxide (POOH) which produces two additional active radicals through homolysis of peroxidic (O-O) bond
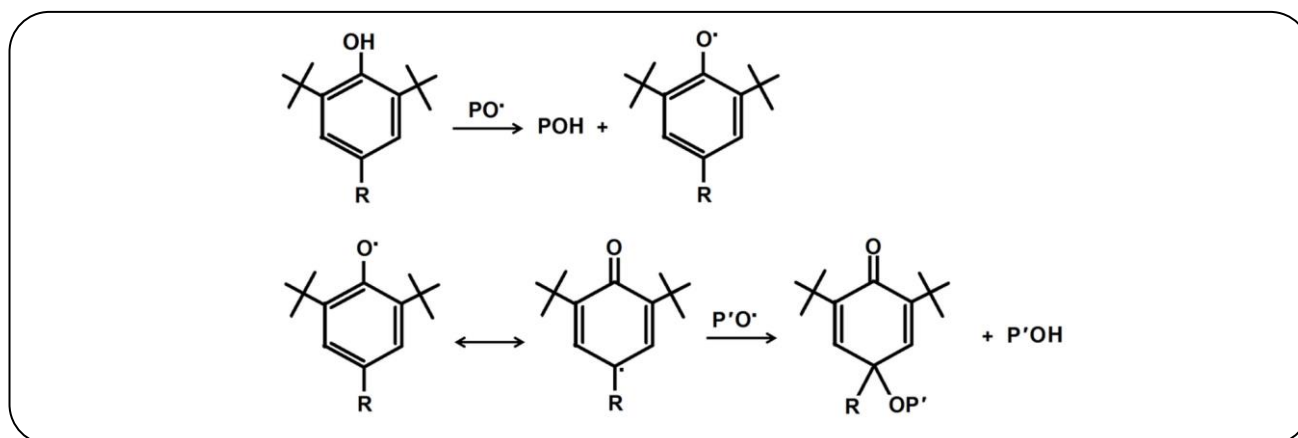
Fig. 1: General mechanism for deactivation of alkoxy radicals by phenolic antioxidants [18].

(the so-called chain branching stage) [8-10]. In oxygen deficient environment the primary alkyl radicals tend towards recombination which results in crosslinking [11, 12]. The incidence of intermolecular crosslinking during melt processing of the polymer leads to viscosity increase which may results in processing difficulties. On the other side, the occurrence of intermolecular crosslinking during service-life leads to reduction of the polymer flexibility and anticipated brittleness of the polymer products. Therefore, PE needs some kind of stabilization for every stage of its life cycle [13-14]. This is generally attained by utilization of given amounts of proper additive or additive systems which deactivate the propagating alkyl and alkyl peroxyl radicals (referred to as primary antioxidants), or decomposes hydroperoxide to inert species (referred to as secondary antioxidants) [15].

Hindered phenols have been used widely as one of the most important primary antioxidants to protect polyethylene during processing as well as in the end application as long-term thermal stabilizers [16-18]. These antioxidants deactivate alkoxy and peroxy radicals by donating a labile phenolic hydrogen atom to the free radicals according to a general stabilization mechanism shown in Fig. 1. So, these antioxidants are known also as chain breaking donor antioxidants. However, transformation of the antioxidant molecules to colored compound during the stabilization mechanism may cause some problems especially in clear polymer items [11]. In addition, they do not immediately stop the auto-oxidation of the polymer as soon as it starts [18]. Furthermore, the increasing performance criteria for the polymeric materials in the modern industry, such as shorter cycle times, more intensive processing conditions necessitate higher stabilization levels. Therefore, during the last decades, many research works have been devoted to generation of new types of antioxidants. Accordingly, efficiency of lactone based systems, hyper-branched antioxidants, antioxidant-grafted polymers and antioxidant-grafted nanoparticles have been evaluated for stabilization of the polymer [19-22].

In the past few years, Jahanmardi and Assempour investigated effects of galbanic acid on thermal and thermo-oxidative degradation of linear low density polyethylene [23]. Results of their study have proven that galbanic acid improves thermo-oxidative stability of the polymer strongly in the solid state and moderately in the melt state. On the basis of their observations, they postulated a mechanism for the thermo-oxidative stabilizing activity of galbanic acid in terms of activity of allylic hydrogen atoms present in its molecular structure. In order to further assess the proposed stabilization mechanism as well as to find new type of antioxidants for polyethylene, the present work was conducted to evaluate thermo-oxidative stability of high density polyethylene (HDPE) in the presence of another model chemical compound having allylic hydrogen atoms present in its molecular structure i.e. 3,3-bis(4-hydroxy-2-methyl-5-propan-2-ylphenyl)-2-benzofuran-1-one, commonly known as thymolphthalein, with a chemical structure shown in Scheme 1 [24]. As it is seen in Scheme 1, thymolphthalein has two phenolic hydrogen atoms in its molecular structure which could participate in its probable free radical deactivating activity [25-27]. So, we eliminate these two hydrogen atoms simply through
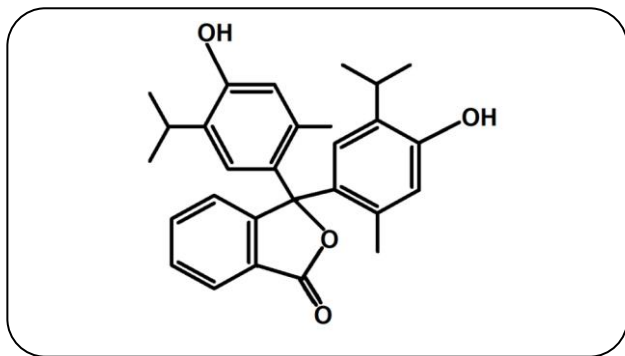
Scheme 1: Molecular structure of thymolphthalein [24].

reaction of thymolphthalein with sodium hydroxide which renders its sodium salt according to the reaction shown in Scheme 2 [28-30]. By comparing stabilization activity of thymolphthalein and that of its sodium salt, the roles of allylic hydrogen atoms and phenolic hydrogen atoms present in its molecular structure could be distinguished.

EXPERIMENTAL SECTION
Materials

The used additive-free HDPE (EX3 grade) with MFI of 0.45 g/10 min, density of 0.945 g/cm^3 and crystalline melting point of 128 °C was supplied as a powder by Arak petrochemical company (Iran). Thymolphthalein with melting point of 253 °C, sodium hydroxide and methanol were obtained from Merck Company (Germany). SONGNOX 1010 with melting point of 118 °C and molecular structure shown in Scheme 3 was supplied by Songwon Industrial Company (South Korea) as a white powder.

Preparation of film samples

HDPE was incorporated with desirable amounts of the selected additives by using solvent premixing. In this method, first of all, we chose methanol as the solvent because of its ability to dissolve all additives and its high volatility at ambient temperature. Then, we dissolved certain amounts of each additive in the solvent and the resulted solutions were poured over HDPE powder, the solvent was then allowed to evaporate for 20 min during stirring. The prepared premixed samples were finally converted into thin films (about 250μm thick) at 190 °C and 100 bar within 4 min using a laboratory hot press. A film of the pure polymer was also prepared as the blank

sample. In addition, a film sample was prepared using sodium salt of thymolphthalein as the additive. Sodium salt of thymolphthalein was prepared by reaction of certain amount of thymolphthalein with 1 M solution of sodium hydroxide in methanol [28-30]. The color of thymolphthalein solutions changes from clear to dark blue in alkaline media. So, observation of the solution color change was used as a simple method to judge if the reaction takes place. Eventually, the obtained dark blue solution containing sodium salt of thymolphthalein was directly used for preparation of corresponding premixed sample. The formulations of the prepared films are given in Table 1. Film samples having each of thymolphthalein, thymolphthalein salt and SONGNOX 1010 alone have been designated as T, S and I, respectively. The film having a mixture of both SONGNOX 1010 and thymolphthalein has been designated as IT. Furthermore, the numerical suffix in the sample designations indicates the weight percentage of the used additive multiplied by 10.

### Evaluation of long-term thermo-oxidative stability of the prepared samples in solid state

Thermo-oxidative stabilities of the HDPE film samples were evaluated using a standard accelerated ageing test which was carried out on 2×4 cm strips of the samples in a forced air-draft oven at 90°C for different periods of time as reported in the literature [32]. The structural changes of the film samples due to oven ageing were followed by taking their FT-IR spectra at different time intervals using a Nicolet FT-IR spectrophotometer (USA). FT-IR spectra taken as an average of 20 scans at a resolution of 4 cm^{-1} in the range of 4000-400 cm^{-1}. The rates of thermo-oxidative degradation of the polymer samples were determined by evaluation of carbonyl index change (ΔCI) at different exposure time intervals, based on the following equation:

$$\Delta CI = CI - CI_0 = A_{(1717)}\big/A_{(2022)} - CI_0 \qquad (1)$$

where, A is the absorbance at the given wavenumber and CI_0 is the original carbonyl index. It should be noted that absorption band at 1717 cm^{-1} arises from stretching vibration of ketonic carbonyl groups. Moreover, absorption band at 2022 cm^{-1}, which arises from the combination of the two vibrational modes of methylene group at 720 and 1303 cm^{-1}, was chosen as an internal thickness band in order to minimize the errors arising
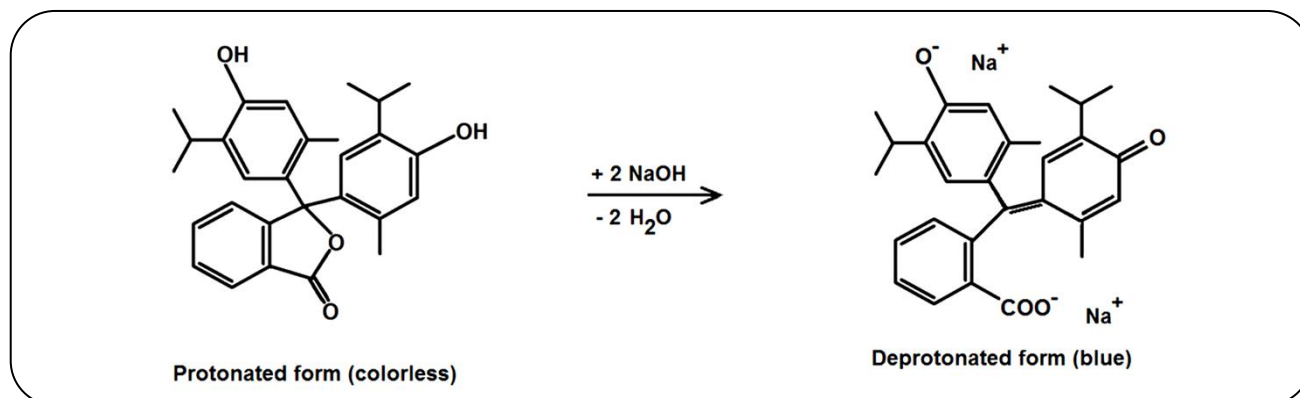
Scheme 2: Reaction of thymolphthalein with sodium hydroxide [30].
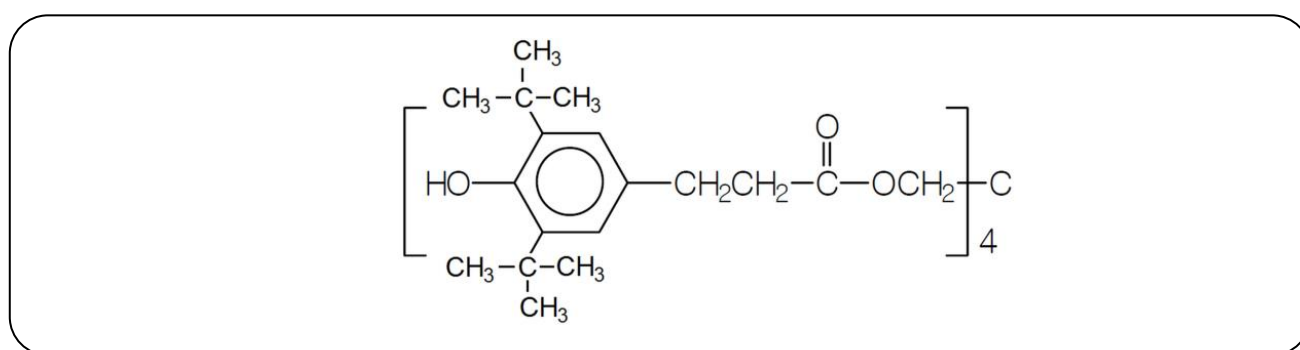
Scheme 3: Molecular structure of SONGNOX 1010 [31].

from the samples thickness [33]. CI_0s were subtracted in order to remove the influence of the original carbonyl groups, so that, the results only stand for the changes took place during the thermal oxidation in the solid state.

Evaluation of thermal-oxidative stability of the prepared samples in melt state

In order to evaluate oxidative resistance of the prepared HDPE samples in the melt state, two different tests, i. e. Oxidation Onset Temperature (OOT) in oxygen atmosphere and Oxidative Induction Time (OIT), were performed.

In the heat-ramp test (OOT), the temperature of each sample (of about 10 mg weight) was raised at a constant rate of 10°C/min from 25°C to 250°C, using a DuPont model 910 DSC thermal analysis system (USA). The samples were kept in oxygen atmosphere with a flow rate of 50 cm^3 /min, from the beginning of the test. The value of Oxidation Onset Temperature (OOT) for each sample was determined from its DSC curves as the temperature corresponding to the deviation from the baseline (onset

of exothermal reaction) [34]. In the isothermal test (OIT), samples of about 10 mg weight were heated in aluminum pans from 25°C to 200°C at 20°C/min under a nitrogen stream in the aforementioned DSC instrument. The nitrogen atmosphere was then changed to oxygen immediately after the temperature was reached and equilibrated at 200°C. Flow rate of the both gases was 50 cm^3 /min according to ASTM D 3895-80. The value of OIT was inferred from DSC curves as the time interval from oxygen introduction until the onset of exothermal reaction.

RESULTS AND DISCUSSION
Long-term thermo-oxidative stability in solid state

Carbonyl groups are the major chemical groups that are formed on polyethylene chain molecules during its oxidation and their presence can be readily determined from their FTIR absorption band at 1800–1700 cm^{-1} [35-37]. So, thermo-oxidative degradation of the HDPE film samples upon ageing at 90°C were assessed by monitoring the changes in their FTIR spectra. The FT-IR spectra of the blank and T1 samples before and

Table 1: Formulation of HDPE film samples.

Sample designation	Blank	T1	T5	T10	I1	IT	S10
HDPE (wt %)	100	100	100	100	100	100	100
Thymolphthalein (wt %)	-	0.1	0.5	1.0	-	0.1	-
Thymolphthalein sodium salt (wt %)	-	-	-	-	-	-	1.0
SONGNOX 1010 (wt %)	-	-	-	-	0.1	0.1	-

Fig. 2: FTIR spectra of the Blank film sample (a) before and (b) after oven aging at 90 °C for 740 h.

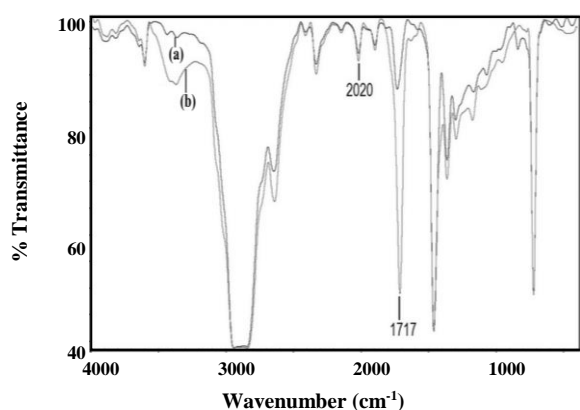*Fig. 3: FTIR spectra of the T1 film sample (a) before and (b) after oven aging at 90 °C for 740 h.*

after ageing for 740 h at 90°C are demonstrated in Figs. 2 and 3, respectively. While, in Fig. 2 the carbonyl absorption band exhibits a drastic growth in intensity upon oven ageing for 740 h, the spectra in Fig. 3 show only a slight evolution of carbonyl groups during the same time of ageing. Therefore, it could be deduced that thymolphthalein plays the role of an effective antioxidant for the polymer at a concentration of 0.1 wt% during oven ageing at the aforementioned conditions.

In order to clarify the efficiency of thymolphthalein in stabilizing the polymer against thermo-oxidative degradation in solid state, the rate of thermal oxidation of all the film samples upon ageing at 90°C was determined by measuring the trend of ΔCI growth in the films through FT-IR analysis and is illustrated in Fig. 4. A characteristic sharp increase of ΔCI for the blank sample is evident in the figure reflecting auto-oxidation after an induction period. On the other hand, only trivial increases in ΔCI are observed for the T1 and T5 samples at prolonged induction periods. In addition, ΔCI for the samples T10 and I1 show no growth even after 740 h of ageing. Thus, one can infer that thymolphthalein at concentrations of 0.1-1.0 wt% has a strong stabilizing
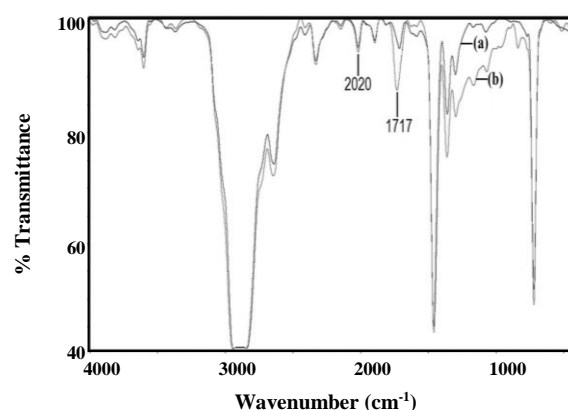
activity during the polymer ageing in solid state which depends on the concentration of the additive. Furthermore, the data illustrated in Fig. 4 shows that no evolution of ΔCI in the IT sample occurs after 740 h of ageing indicating that thymolphthalein at a concentration of 0.1 wt% does not interfere with the stabilizing efficiency of SONGNOX 1010 in the polymer. On the other hand, SONGNOX 1010 acts as a chain breaking donor antioxidant in polyethylene as it was illustrated in Fig. 1. So, it seems that thymolphthalein is not likely to be a chain breaking acceptor antioxidant which deactivates free radicals through abstraction of labile hydrogen atoms from these species. On the other side, comparing the oxidative degradation rates of the blank, T10 and S10 samples in Fig. 4 confirms that sodium salt of thymolphthalein at a concentration of 1.0 wt% has a strong auto-retardation effect on the polymer oxidation in the solid state and its efficiency in this respect is similar to that of thymolphthalein. This observation implies that phenolic hydrogen atoms of thymolphthalein which are absent in the molecular structure of the sodium salt, don't play the principal role in the stabilization action of both thymolphthalein and its sodium salt.
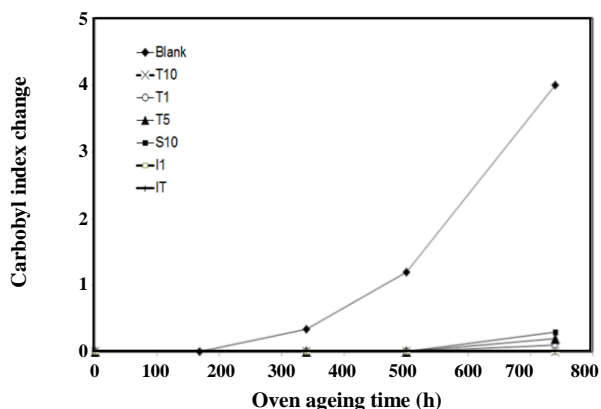
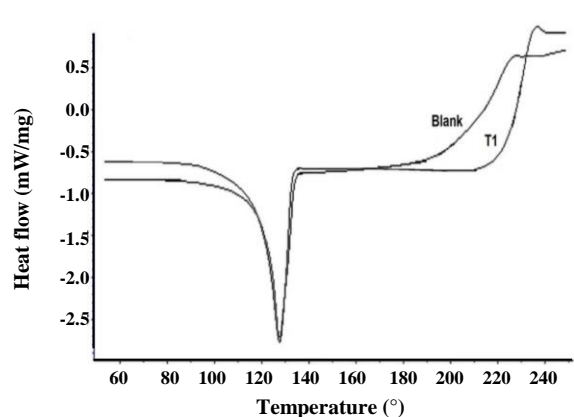**Fig. 4: Variations of carbonyl index change (ΔCI) for the HDPE films in terms of oven ageing time at 90°C.**

Fig. 6: The values of oxidation onset temperature (OOT) obtained for the HDPE samples.

Fig. 5: The DSC curves of the Blank and T1 samples obtained in the heat-ramp experiments.
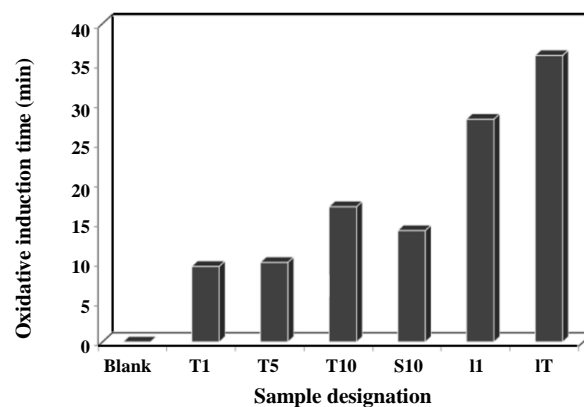
Fig. 7: The values of oxidative induction time (OIT) obtained for the HDPE samples.

Thermo-oxidative stability in melt state

Thermal oxidation of polyethylene in melt state is an exothermic chain reaction whose occurrence could be readily detected by thermal or calorimetric methods. Hence, thermo-oxidative stability of the HDPE samples in the melt state was assessed by Differential Scanning Calorimetry (DSC). The DSC thermograms of the blank and the T1 samples are shown in Fig. 5. As it is evident in the figure, the endothermic peak due to the melting of the neat polymer at 128°C remains unchanged for the T1 sample. However, the onset of the exothermic peak of the polymer oxidation which is about 174°C for the blank sample is shifted to 210°C after the addition of thymolphthalein for the T1 sample. So, it could be inferred that thymolphthalein at a concentration of 0.1 wt% plays the role of an efficient antioxidant for the polymer in the melt state.
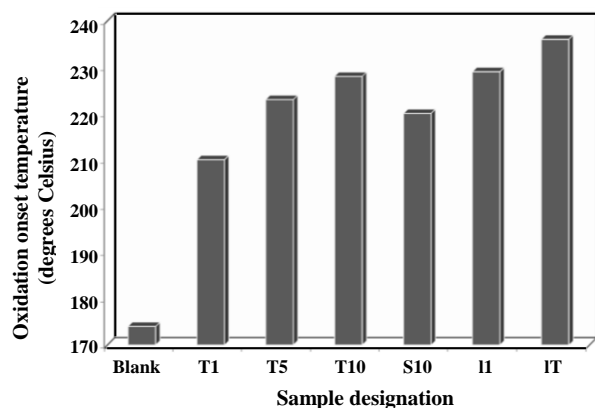
In order to quantify the effect of the additives in stabilizing the polymer against thermo-oxidative degradation in the melt state, the temperature corresponding to the deviation from the baseline (onset of thermal oxidation) which is defined as Oxidation Onset Temperature (OOT) was measured for all the samples. Values of OOT and Oxidative Induction Time (OIT) for polyethylene could be regarded as two important characteristics of the polymer stability against oxidative degradation in melt state. Hence, value OIT of for the samples was also determined from DSC curves obtained in isothermal tests as the time interval from oxygen introduction until the onset of the exothermal reaction. The measured values of OOT and OIT for all the samples are given in Figs. 6 and 7, respectively. As it can be seen in these figures, the both OIT and OOT values have been remarkably increased in the cases of T1, T5

and T10 samples, respectively, in relation to the blank sample. This observation indicates that thymolphthalein operates an antioxidant role in the polymer melt and its stabilizing effect is increased with increasing its concentration. However, the amounts of the modifications in OIT and OOT values of the polymer in the presence of thymolphthalein alone are less than those obtained in the presence of SONGNOX 1010 alone. Moreover, both OIT and OOT values of IT sample which contains both thymolphthalein and SONGNOX 1010 are greater than those of I1 sample, respectively. So, it could be inferred that thymolphthalein doesn't interfere the stabilization action of SONGNOX 1010 in the polymer. Hence, it could be deduced again thymolphthalein probably plays the role of a chain breaking donor antioxidant. On the other hand, by comparing *OIT* and *OOT* values of T10 and S10 samples, it is seen that the sodium salt of thymolphthalein can stabilize the polymer against oxidative degradation in melt state and its efficiency in this regard is slightly less than that of thymolphthalein. So, again one can conclude that phenolic hydrogen atoms of thymolphthalein don't play the main role in stabilization action of both thymolphthalein and its sodium salt.

Probable mechanism for the stabilization action of thymolphthalein

Considering the results obtained through investigating thermo-oxidative degradation of the HDPE films in both solid and melt states, one can deduce that thymolphthalein is capable to play the role of an efficient antioxidant in the polymer during its service life as well as its processing at high temperatures. Although, it is difficult to discover the exact mechanism through which thymolphthalein influences thermo-oxidation stability of HDPE, but on the basis of the above mentioned observations and inferences, here we try to find out probable set of reactions which are involved in the stabilization action of the additive.

As thymolphthalein plays the role of a chain breaking donor, its molecules should have hydrogen atoms that could be readily abstracted by free radical species (P˙) generated in thermal oxidation of the polymer. Two types of labile hydrogen atoms could be identified in molecular structure of thymolphthalein,

i. e. phenolic and allylic 3° hydrogen. As it was shown that phenolic hydrogen atoms of thymolphthalein don't play the main role in stabilization action of thymolphthalein, the allylic 3° hydrogen atoms could be regarded as the main hydrogen atoms that take part in the reactions resulting in the stabilization of the polymer. It should be mentioned that through investigating effects of galbanic acid on thermo-oxidative stability of LLDPE, Jahanmardi and Assempour proposed a similar activity for allylic hydrogen atoms present in molecular structure of galbanic acid [24]. As illustrated in Fig. 8, at the first step of stabilization mechanism of the additive, the free radical species (P˙) may be deactivated by abstracting an allylic 3° hydrogen atom from each of the two phenolic parts of thymolphthalein. The thymolphthalein radical which is thus produced could be stabilized through resonance by pi electrons present in the adjacent phenyl ring and could deactivate another radical (P' ˙) [38]. This process may be iterated on one molecule of thymolphthalein and so, more radicals are deactivated. However, the slightly lower efficiency of thymolphthalein in stabilizing the polymer in comparison with that of SONGNOX 1010 implies that the radical species of thymolphthalein are removed from the system through recombination reactions or they probably take part in one or more unknown reactions especially involving hydrogen atoms of two methyl groups attached to the allylic 3° radicals.

CONCLUSIONS

In this work, effects of thymolphthalein on thermo-oxidative stability of HDPE in both solid and melt states was investigated. On the basis of the obtained results, it could be concluded that thymolphthalein plays the role of an efficient antioxidant in HDPE during service life of the polymer as well as its melt processing. The efficiency of this new antioxidant in stabilizing the polymer against thermal oxidation in solid state depends on its concentration and was shown to be comparable to that of the commercially used antioxidant, SONGNOX 1010. However, the thermo-oxidative stabilization efficiency of the additive in melt state is not as outstanding as that of SONGNOX 1010. Moreover, it was suggested that thymolphthalein acts as a chain breaking donor antioxidant and its activity
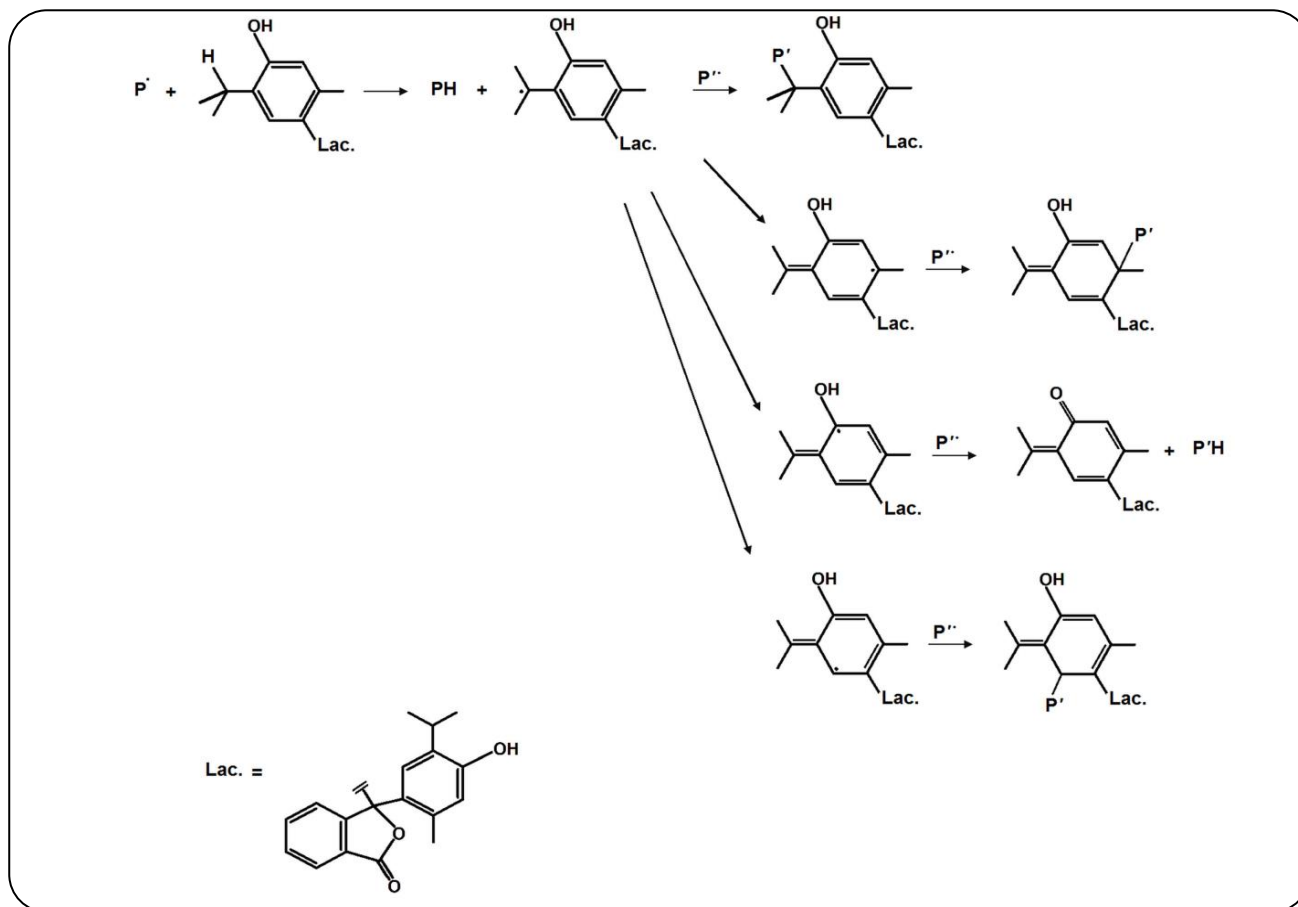
Fig. 8: Possible reactions responsible for the thermo-oxidative stabilization action of thymolphthalein.

could be attributed to the activity of several allylic 3° hydrogen atoms present in its molecular structure.

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