

Evaluation of effects of thymolphthalein on thermo-oxidative stability of polypropylene

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ABSTRACT

The present work is aimed to find a new and efficient type of antioxidants for polypropylene. Hence, effects of 3,3-bis(4-hydroxy-2-methyl-5-propan-2-ylphenyl)-2-benzofuran-1-one, generally known as thymolphthalein, on thermo-oxidative stability of polypropylene in solid and melt states were evaluated and compared with those of SONGNOX 1010, an efficient commercially used antioxidant for the polymer. Oven ageing experiments followed by Fourier transform infrared (FTIR) spectroscopy showed that thymolphthalein increased thermo-oxidative stability of the polymer outstandingly in the solid state and its stabilization efficiency was comparable to that of SONGNOX 1010. In addition, measurements of oxidative induction time (OIT) and oxidation onset temperature (OOT) revealed that thymolphthalein improved thermo-oxidative stability of the polymer in the melt state significantly. It was also observed that thymolphthalein did not interfere with the stabilization action of SONGNOX 1010 in the polymer neither in melt nor in solid state. On the basis of the obtained results, a probable mechanism for the stabilization action of thymolphthalein in the polymer is proposed. **Polyolefins J (2017) 4: 79-86**

Keywords: Antioxidant; degradation; polypropylene; stabilization.

INTRODUCTION

During the past decades, a vast amount of studies have been carried out related to thermo-oxidative degradation of polypropylene (PP) as well as stabilization of this commodity polymer against thermal oxidation [1]. Thermo-oxidative degradation of PP during high-temperature melt processing as well as its solid state weathering proceeds via a free radical chain reaction

(the so-called autoxidation) which alters chemical structure of the polymer through generation of different oxidation groups such as acids, ketones, and so forth [2]. The worst feature of the process is formation of hydro-peroxide (POOH) which produces two additional active radicals (i.e., macro-alkoxy and hydroxyl radicals) through breakage of peroxidic (O-O) bond (the so-called chain branching stage) [3]. The produced macro-alkoxy radical may convert to ketone

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via a main-chain scission reaction which also reduces the molecular weight of the polymer. Reduction of the polymer molecular weight results in weakening of the mechanical properties of the polymer which is manifested by brittleness of the polymer products. Therefore, PP needs some kinds of stabilization against thermal oxidation for each stage of its life cycle. This is generally achieved by utilization of given amounts of proper additives which deactivate the radicals (referred to as primary antioxidants), or decompose hydro-peroxide to inert species (referred to as secondary antioxidants) [4].

Hindered phenols have been used widely as one of the most important primary antioxidants to protect PP during processing as well as in the final application as long-term thermal stabilizers [5, 6]. These antioxidants deactivate the propagating radicals by donating a labile phenolic hydrogen atom to the radicals according to a general stabilization mechanism shown in Figure 1. So, these antioxidants are known also as chain breaking donor antioxidants. However, these strong antioxidants suffer from some drawbacks; for instance, transformation of the antioxidant molecules to a colored compound during the stabilization mechanism may change the polymer's color which, in turn, could cause some problems especially in clear polymer artifacts [7]. Furthermore, the increasing performance criteria for the polymeric materials in the modern industry, such as shorter processing cycle times and more intensive processing conditions require higher stabilization levels. Hence, during the recent decades, many scientific and technical efforts have been devoted to discovering new types of antioxidants. Accordingly, efficacy of in situ stabilization by lignin, antioxidant-grafted polymers and antioxidant-

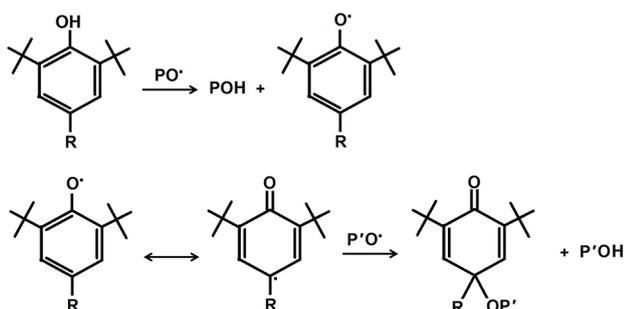
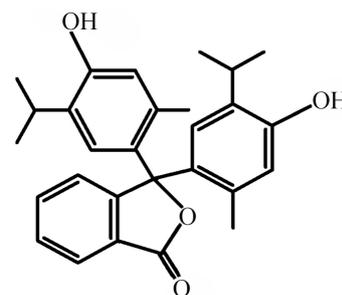


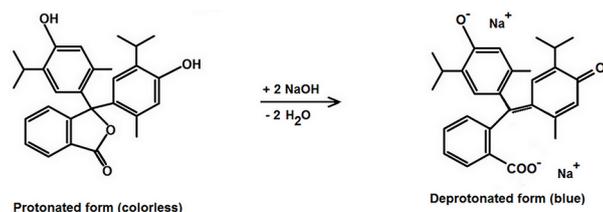
Figure 1. Generally accepted mechanism for deactivation of alkoxy radicals by phenolic antioxidants [5].

grafted nanoparticles in thermo-oxidative stabilization of the polymer has been evaluated [8-10].

Recently, Jahanmardi and Assempour studied effects of galbanic acid on thermal and thermo-oxidative degradation of linear low density polyethylene [11]. Results of the study proved that galbanic acid improved thermo-oxidative stability of the polymer strongly in the solid state and moderately in the melt state. They also postulated a mechanism for the stabilizing action of galbanic acid, in which allylic hydrogen atoms present in its molecular structure, played the main role. In order to further evaluate the proposed stabilization mechanism as well as finding new category of antioxidants for PP, the present work was performed to study thermo-oxidative stability of PP 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, generally known as thymolphthalein, with a molecular structure shown in Scheme 1 [12]. As it can be seen in Scheme 1, thymolphthalein has two phenolic hydrogen atoms in its chemical structure which may participate in its probable stabilization activity. However, these two hydrogen atoms could be simply eliminated through reaction of thymolphthalein with sodium hydroxide, which rendered sodium salt of thymolphthalein according to the reaction shown in Scheme 2 [13]. Thus, through comparing stabilization efficiency of thymolphthalein and that of its sodium salt, the roles of allylic hydrogen atoms (which are better referred as benzylic hydrogen atoms) and phenolic hydrogen atoms present in molecular structure of thymolphthalein could be distinguished. Accordingly, Jahanmardi et al. showed that sodium salt of thymolphthalein at a concentration of 1.0 wt% had strong stabilization ef-



Scheme 1. Molecular structure of thymolphthalein [12].



Scheme 2. Reaction of thymolphthalein with sodium hydroxide [13].

fects on the oxidation of polyethylene in solid and melt states and its efficiencies in these respects were shown to be similar to those of thymolphthalein [14]. Hence, they concluded that phenolic hydrogen atoms of thymolphthalein which are absent in the molecular structure of its sodium salt, did not play the main role in the stabilization action of thymolphthalein in polyethylene. Regarding the above mentioned findings, evaluation of thermo-oxidative stabilization efficiency of sodium salt of thymolphthalein in polypropylene was omitted in the present work and the study focused on the stabilization activity of thymolphthalein itself in polypropylene.

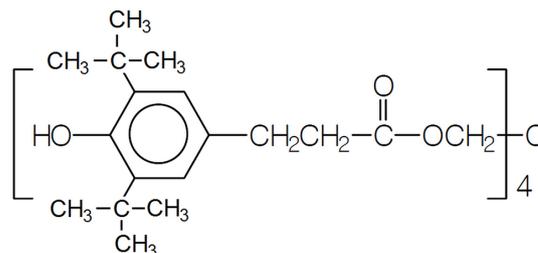
EXPERIMENTAL

Materials

The used PP (HP510M grade) with MFI of 9.0 g/10 min, density of 0.9 g/cm³ and crystalline melting point of 167°C was obtained from Jam Petrochemical Company (Iran). Thymolphthalein with melting point of 253°C and methanol were purchased from Merck Company (Germany). SONGNOX 1010, as a white powder, with melting point of 118°C and molecular structure shown in Scheme 3 was obtained from Songwon Industrial Company (South Korea) [5].

Preparation of film samples

PP was mixed with desirable amounts of the selected additives at 190°C in a Brabender internal mixer within a period of 6 min, at a rotor speed of 60 rpm. The



Scheme 3. Molecular structure of SONGNOX 1010 [5].

prepared samples were then converted to thin films with a thickness of about 200 μm 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. The formulations of the prepared film samples are given in Table 1. The film samples having each of thymolphthalein and SONGNOX 1010 alone have been designated as T and S, respectively. The film sample having a mixture of both SONGNOX 1010 and thymolphthalein has been designated as T+S.

Evaluation of thermo-oxidative stability of the prepared film samples

Thermo-oxidative stability in solid state

Thermo-oxidative stability of the prepared PP film samples was evaluated using a standard accelerated ageing test which was carried out on 4×8 cm strips of the samples in a forced air-draft oven at 90°C for different periods of time. The chemical changes of the film samples due to oven ageing were followed by taking their FTIR spectra at different time intervals using a PerkinElmer FTIR spectrophotometer (USA). FTIR spectra were taken as 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 prepared film samples were specified by evaluation of carbonyl index (CI) at different aging time intervals, according to the following equation:

$$CI = A_{(1717)} / A_{(905)} - CI_0 \quad (1)$$

where, A is the absorbance at the given wavenumber

Table 1. Formulation of PP film samples.

| Sample designation | Blank | T0.1% | T0.2% | T0.5% | T1% | S0.1% | T+S |
|------------------------|-------|-------|-------|-------|-----|-------|-----|
| PP (wt %) | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Thymolphthalein (wt %) | - | 0.1 | 0.2 | 0.5 | 1.0 | - | 0.1 |
| SONGNOX 1010 (wt %) | - | - | - | - | - | 0.1 | 0.1 |

and CI_0 is the initial carbonyl index. Absorption band at 905 cm^{-1} was chosen as an internal thickness band in order to minimize the errors arising from the samples thickness [15]. CI_0 s were subtracted in order to eliminate the effect of the initial carbonyl groups, so that, the results only represent the changes occurred during the thermal oxidation in the solid state.

Thermo-oxidative stability in melt state

In order to assess oxidative resistance of the prepared samples in the melt state, two different tests i.e., oxidation onset temperature (OOT) in oxygen atmosphere and oxidative induction time (OIT), were carried out. In the OOT test, the temperature of each sample (of about 10 mg weight) was elevated at a constant rate of $10^\circ\text{C}/\text{min}$ from 25°C to 250°C , using a Zufa model ZF-DS-D2 DSC thermal analysis system (China). The samples were kept in an oxygen atmosphere with a flow rate of $50\text{ cm}^3/\text{min}$, from the commencement of the test. The amount of oxidation onset temperature (OOT) for each sample was specified from its DSC curves as the temperature corresponding to the deviation from the baseline (inception of exothermal oxidative chain reaction) [16]. In the OIT test, samples of about 10 mg weight were heated in aluminum pans from 25°C to 200°C at $20^\circ\text{C}/\text{min}$ under a nitrogen flow in the previously mentioned DSC instrument. The nitrogen atmosphere was then altered to oxygen instantly after the temperature was reached and equilibrated at 200°C . Flow rate of the both gases was $50\text{ cm}^3/\text{min}$ pursuant to ASTM D 3895-80. The value of OIT was deduced from DSC curves as the time interval from oxygen introduction until the onset of exothermal oxidation reaction.

RESULTS AND DISCUSSION

Long-term thermo-oxidative stability in solid state

Carbonyl groups are the most important chemical groups formed on PP molecules during oxidation and their presence can be simply determined from their FTIR absorption band at $1800\text{--}1700\text{ cm}^{-1}$ [2, 17]. Hence, thermal oxidation of the prepared film samples due to ageing at 90°C was evaluated by tracking the

changes in their FTIR spectra. The FTIR spectra of the blank and T0.1% samples before and after ageing for 1200 h at 90°C are exhibited in Figures 2 and 3, respectively. Whilst, the carbonyl absorption band in Figure 2 shows a significant growth due to oven ageing for 1200 h, the spectra in Figure 3 indicate no increase of carbonyl groups during the same time of ageing. Therefore, it can be inferred that thymolphthalein plays the role of an efficient antioxidant for PP at a concentration of 0.1 wt% during oven ageing at 90°C .

In order to elucidate the efficiency of thymolphthalein in thermo-oxidative stabilization of PP in solid state, the rate of the thermal oxidation of all the film samples at 90°C was determined through measuring CI for the films from their FTIR spectra taken at different time intervals during the ageing. The measured CI values are illustrated in Figure 4 in terms of oven ageing time. An intense increase of CI for the blank sample is seen in the figure indicating auto-oxidation of the polymer after an induction period. On the other hand, no growth in CI value of all other samples is seen even after 2000 h of ageing. Thus, it can be deduced that thymolphthalein at concentrations of 0.1–1.0 wt% performs a significant stabilization function during the polymer ageing in solid. Moreover, the data presented in Figure 4 shows that no evolution of carbonyl groups in the T+S sample happens after 2000 h of ageing indicating that thymolphthalein at a concentration of 0.1 wt% does not interfere with the stabilization function of SONGNOX 1010 in the polymer during the course of oven ageing. Since SONGNOX 1010 acts as a chain breaking donor antioxidant in

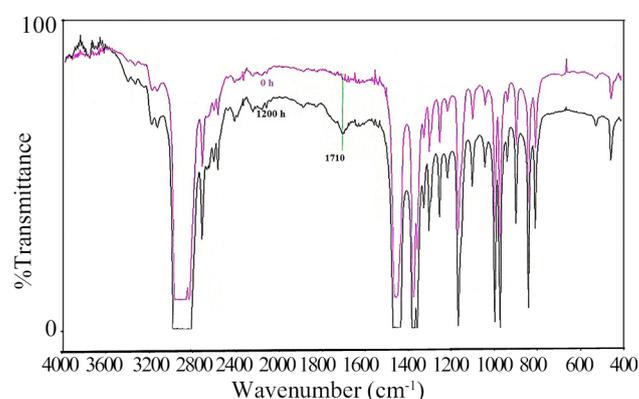


Figure 2. FTIR spectra of blank film sample before and after oven aging at 90°C for 740 h.

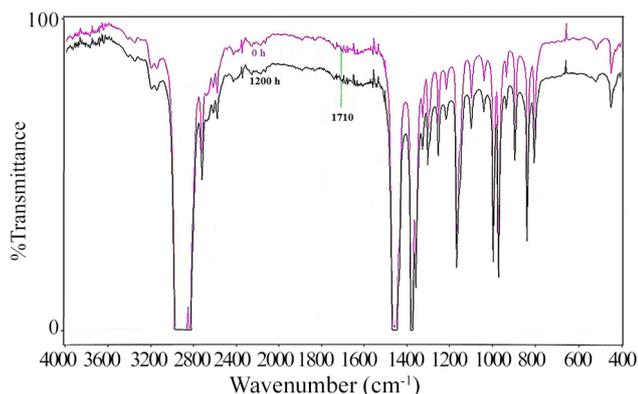


Figure 3. FTIR spectra of T0.1% film sample before and after oven aging at 90°C for 740 h.

PP, thymolphthalein is not likely a chain breaking acceptor antioxidant, but it is expected to deactivate free radicals through abstraction of labile hydrogen atoms from these species [14].

Thermo-oxidative stability in melt state

Thermal oxidation of PP in melt state is an exothermic reaction whose incidence could be simply discovered by calorimetric methods. Thus, thermo-oxidative stability of the PP samples in the melt state was evaluated by differential scanning calorimetry (DSC). The DSC curves of the blank and the T0.1% samples are illustrated in Figure 5. As it is seen in the figure, the endothermic peak due to the melting of the pure polymer at 167°C remains unaltered for the T0.1% sample. However, the onset of the exothermic peak of the polymer oxidation which is about 199°C for the blank sample is moved to 221°C by the addition of 0.1 wt% of thymolphthalein. So, it could be directly deduced that thymolphthalein at a concentration of 0.1 wt% played the role of an effective antioxidant for the polymer in

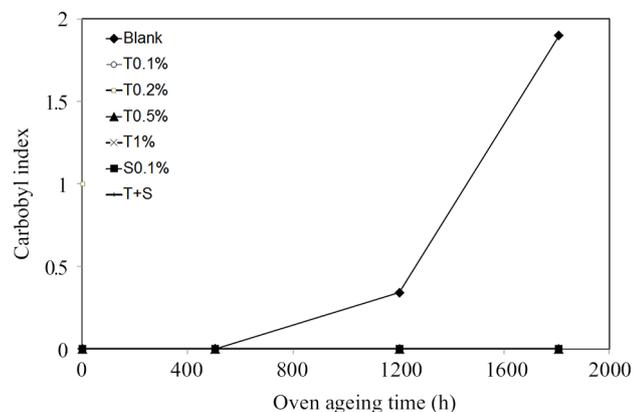
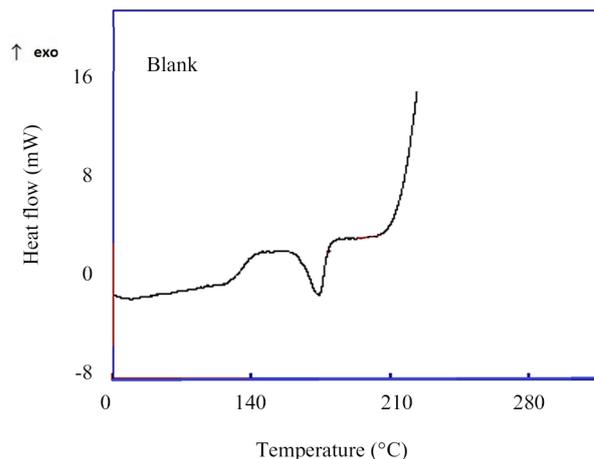
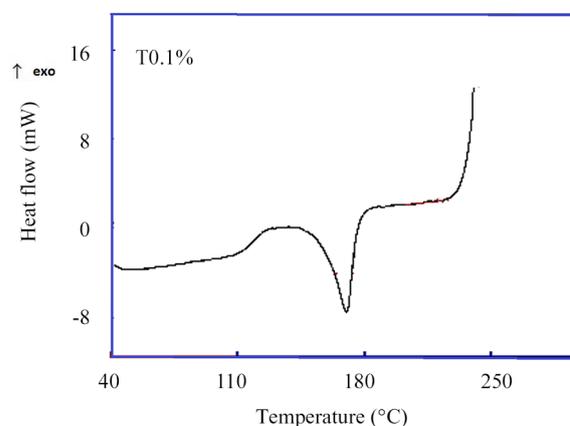


Figure 4. Variations of carbonyl index (CI) of PP films in terms of oven ageing time at 90°C.



(a)



(b)

Figure 5. DSC curves of the blank and T0.1% samples obtained in the heat-ramp experiments.

the melt state.

In order to clarify the effect of thymolphthalein in stabilizing the polymer against thermal oxidation in the melt state, the temperature corresponding to the deviation from the baseline (onset of thermal oxidation), defined as oxidation onset temperature (OOT), was measured for all the samples. Moreover, oxidative induction time (OIT) for all the samples was also determined from DSC curves obtained in isothermal tests as the interval from oxygen introduction until the commencement of the exothermal reaction. Values of OOT and OIT for PP are regarded as two important characteristics of the polymer stability against oxidative degradation in melt state. The measured values of OOT and OIT for all the samples are presented in Figures 6 and 7, respectively. As it is seen in the figures, both OIT and OOT values have been consider-

ably increased in the cases of T0.1%, T0.5%, and T1% samples, respectively, compared to the blank sample. This observation suggests that thymolphthalein plays the role of an antioxidant in the polymer melt. However, the amount of stabilization is not proportional to the amount of thymolphthalein incorporated in the samples. This can be explained in terms of poor distribution of thymolphthalein in PP which is due to the fact that melting point of thymolphthalein is above the processing temperature of the polymer and therefore, a part of the additive remains solid during the melt processing of the polymer and cannot take part in the stabilization function. In addition, the amount of thymolphthalein that dissolves in PP and takes part in the stabilization of the polymer does not increase proportionally with the overall concentration of thymolphthalein in the samples. This is because of low solubility of thymolphthalein in PP which is due to their dissimilar polarities. So, it seems that in order to overcome the problem, it is necessary to modify the chemical structure of the additive through assembling a long hydrocarbon chain onto molecular structure of thymolphthalein, e.g., via an esterification reaction between the phenolic groups present in its molecule and a fatty acid.

Moreover, the amounts of the improvement in OIT and OOT values of the polymer in the presence of 0.1% by weight of thymolphthalein alone (in the case of T0.1%) are similar to those obtained in the presence of 0.1% by weight of SONGNOX 1010 alone (in the case of S0.1%). However, an interesting finding is that the both OIT and OOT values of T+S sample are

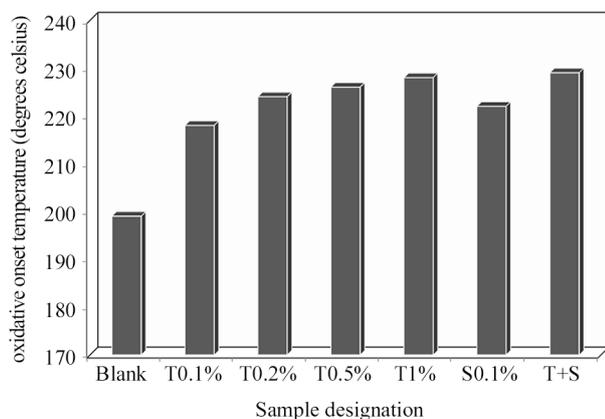


Figure 6. values of oxidation onset temperature (OOT) obtained for PP samples.

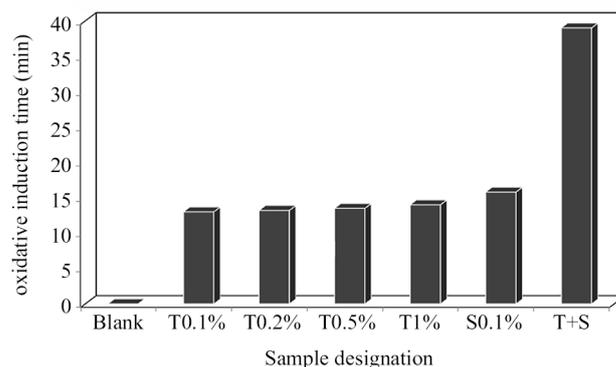


Figure 7. values of oxidative induction time (OIT) obtained for PP samples.

greater than those of T0.1% and S0.1% samples, respectively. So, it can be deduced that not only thymolphthalein does not disturb the stabilization function of SONGNOX 1010 in the molten polymer but also, a synergism between the two additives is observed.

A possible mechanism for the stabilization action of thymolphthalein

Although, it needs more evidences to propose the exact mechanism through which thymolphthalein enhances thermo-oxidation stability of PP, but on the basis of the aforementioned findings and inferences, here we want to suggest a set of reactions which are likely associated with the stabilization mechanism of the additive. The proposed mechanism is illustrated in Figure 8. As it was mentioned earlier, phenolic hydrogen atoms of thymolphthalein have been shown to play an unessential role in its stabilization action [14]. So, the benzylic 3° hydrogen atoms could be regarded as the main hydrogen atoms that are donated to free radicals during the stabilization of the polymer [11]. As it is seen in Figure 8, at the first step of stabilization mechanism of the additive, thymolphthalein could deactivate a free radical (P') through donating a benzylic 3° hydrogen atom from each of its two phenolic parts. The situation of the radical which is so formed on thymolphthalein molecule could be delocalized through resonance by pi electrons present in the adjacent phenyl ring. The thymolphthalein radical which is thus stabilized might deactivate another radical (P') through either donating another hydrogen atom or recombination. The above-mentioned process might be repeated on the same molecule of thymolphthalein and so, more radicals could be deactivated by only one molecule of the additive.

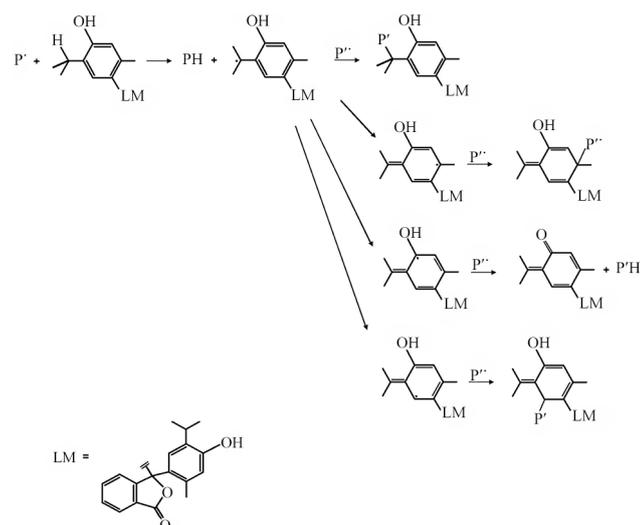


Figure 8. Possible reactions responsible for the thermo-oxidative stabilization action of thymolphthalein.

CONCLUSION

In this work, effects of thymolphthalein on thermo-oxidative stability of PP in both solid and melt states were investigated. The efficiency of this new antioxidant in stabilizing the polymer against thermal oxidation in both melt and solid states was shown to be comparable to that of the commercially used antioxidant, SONGNOX 1010. Hence, thymolphthalein is expected to play the role of an efficient antioxidant in the polymer during its service life as well as its processing at high temperatures. Moreover, according to the obtained results, it was deduced that thymolphthalein acted as a chain breaking donor antioxidant and its activity could be attributed to the activity of two benzylic 3° hydrogen atoms present in its molecular structure. Accordingly, a probable mechanism for the thermo-oxidative stabilization action of the additive in the polymer was proposed.

REFERENCES

- Bertin D, Leblanc M, Marque SRA, Siri D (2010) Polypropylene degradation: Theoretical and experimental investigations. *Polym Degrad Stabil* 95: 782-791
- Gugumus F (2002) Re-examination of the thermal oxidation reactions of polymers 3. Various reactions in polyethylene and polypropylene. *Polym Degrad Stabil* 77: 147-155
- Ying Q, Zhao Y, Liu Y (1991) A study of thermal oxidative and thermal mechanical degradation of polypropylene. *Makromol Chem* 192: 1041-1058
- Wang X, Wang B, Song L, Wen P, Tang G, Hua Y (2013) Antioxidant behavior of a novel sulfur-bearing hindered phenolic antioxidant with a high molecular weight in polypropylene. *Polym Degrad Stabil* 98: 1945-1951
- Voigt W, Todesco R (2002) New approaches to the melt stabilization of polyolefins. *Polym Degrad Stabil* 77: 397-402
- Richaud E, Fayolle B, Verdu J (2011) Polypropylene stabilization by hindered phenols - Kinetic aspects. *Polym Degrad Stabil* 96: 1-11
- Allen N S, Edge M (1992) *Fundamentals of polymer degradation and stabilization*. 3rd ed., Elsevier, 22-51
- Marques M, Oliveira R, Araujo R, Amantes B (2014) In situ stabilization of polypropylene by lignin using a Ziegler-Natta catalyst. *Polyolefins J* 1: 17-24
- Kim T H, Oh DR (2004) Melt grafting of maleimides having hindered phenol antioxidant onto low molecular weight polyethylene. *Polym Degrad Stabil* 84: 499-503
- Shi X, Wang J, Jiang B, Yang Y (2013) Hindered phenol grafted carbon nanotubes for enhanced thermal oxidative stability of polyethylene. *Polymer* 54: 1167-1176
- Jahanmardi R, Assempour H (2008) Effects of galbanic acid on thermal and thermo-oxidative stabilities of LLDPE. *Iran Polym J* 17: 799-806
- Sabnis RW (2007) *Handbook of acid-base indicators*. CRC Press, 361-390
- Abbehausen C, Formiga ALB, Sabadini E, Yoshida IVP (2010) A β -cyclodextrin/siloxane hybrid polymer: Synthesis, characterization and inclusion complexes. *J Braz Chem Soc* 21: 1867-1876
- Jahanmardi R, Pourattar P, Soleimani H, Shohani N (2016) Effects of thymolphthalein on thermo-oxidative stability of high density polyethylene in melt and solid states. *Iran J Chem Chem Eng*, in press

- 15- Yang R, Liu Y, Yu J, Wang K (2006) Thermal oxidation products and kinetics of polyethylene composites. *Polym Degrad Stabil* 91: 1651-1657
- 16- Zeynalov E B, Allen N S (2006) Modelling light stabilizers as thermal antioxidants. *Polym Degrad Stabil* 91: 3390-3396
- 17- Mohammadhosseini M, Jahanmardi R (2014) Investigating effect of ferric stearate on stabilization efficiency of a phenolic antioxidant during thermal oxidation of polyethylene. *Iran Polym J* 23: 801-807