

Fullerenes C₆₀/C₇₀ and C₇₀ as Antioxidants for Polystyrene

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ABSTRACT

Two-step investigation was made to determine the antioxidant properties of fullerenes C₆₀/C₇₀ and C₇₀ in polystyrene. The antioxidative activity of fullerene C₆₀/C₇₀ has been studied by model reaction of the initiated oxidation of styrene and then in accelerated tests of C₆₀/C₇₀ and C₇₀ mixtures with polystyrene. It was established that the initiation and oxidation rates of the model reaction is substantially reduced in the presence of C₆₀/C₇₀. The rate constant for the addition of styryl radicals to C₆₀/C₇₀ was determined as $k_{(333\text{ K})} = (9.0 \pm 1.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. By differential scanning calorimetry (DSC) and thermogravimetry (TGA) it was demonstrated that fullerenes show a stabilizing effect comparable with the influence of the sterically-hindered phenol Irganox 1010 and amine Agerite White. The suggestion was made that the retarding effect of fullerenes is connected with its interaction with macroradicals R· leading to formation of less active compounds.

Key Words:

fullerene C₆₀/C₇₀;
antioxidant;
polystyrene;
thermo-oxidative degradation;
kinetics.

INTRODUCTION

The idea about using fullerenes as effective radical terminators in chain reactions that is as efficient inhibitors of radical polymerization or stabilizers for polymer materials was originated from high electron affinity of fullerenes. Electron affinities were

calculated for C₆₀ through C₈₄ [1] and these are shown in Table 1.

A quick glance at these values clearly shows that fullerenes should easily accept electrons and free radicals, and thus they were expected to play significant role in radical

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Table 1. Estimated electron affinities of fullerenes [1].

Fullerenes	Electron affinities (eV)
C ₆₀	2.7
C ₇₀	2.8
C ₇₆ (D ₂ isomer)	3.2
C ₇₈ (C _{2v} isomer)	3.4
C ₈₂ (C ₂ isomer)	3.5
C ₈₄ (D ₂ isomer)	3.5
C ₈₄ (D _{2d} isomer)	3.3

processes [2,3].

It becomes very obvious if we consider a general scheme of these reactions (polymerization, degradation, oxidation, and cracking):

Chain initiation: generation of primary radicals R₍₀₎ (W₁ is initiation rate)

Chain propagation: RH + R₍₀₎ → R_(n) (k_p)

Chain termination: 2 R_(n) → inactive products (k_t)

Where, RH: substrate, k: reaction rate constant, and R_(n): - radicals leading the reaction chain.

It will be seen from the above reactions that fullerene should markedly influence the course of chain reactions.

The facile addition of some alkyl radicals to fullerenes was confirmed also by high magnitudes of the addition rate constants = 10⁷-10⁹ M⁻¹s⁻¹ obtained in works [4-6].

Thus, taking into consideration a high concentration of alkyl radicals usually available in polymers during radical degradation it was immensely interesting to use fullerenes as antioxidant-stabilizers for polymers.

In previous work we had already studied the stabilizing effect of fullerene C₆₀ and showed it as purely comparable with influence of the steric hindered phenol Irganox1076 [6].

In addition, the chemiluminescence investigation of thermo-oxidative degradation of polyethylenes HDPE, LDPE and LLDPE stabilized with various carbon materials: fullerene C₆₀, three adducts with levopimaric acid, two sorts of carbon black and nanocarbon was recently reported [7]. Interesting work concerning the retardation of oxidation of polystyrene, polyethylene, polypropylene and poly(vinylidene fluoride) by carbon nanotubes has been just published by

discoverer of fullerenes Sir Harry Kroto and co-authors [8]. They have shown that the incorporation of boron into nanotubes enhances the electron affinity of the tubes and leads to a small increase in antioxidant efficiency.

In the present paper we continue the investigations to examine the stabilizing effect of fullerenes, C₆₀/C₇₀ and C₇₀ for thermooxidative degradation of polystyrene.

Theoretical Considerations

Testing of chemical compounds as stabilizers for polymers usually starts with preliminary quantitative estimation of their chemical activities by means of model oxidation reactions of some hydrocarbons [9-11].

The theoretical basis for the use of the low-molecular compounds as models is the similarity of oxidation mechanisms for hydrocarbons and carbon-chain polymers [11,12].

The inhibiting efficiency of a chemical compound as a potential stabilizer is a function of its capacity of hindering the initiation of chain oxidation [11]. Various chemical parameters characterizing the process of retardation can be used as criteria for quantitative estimation of an antioxidant efficiency, for instance, the ratio of reaction rates in the absence and presence of the tested compound, induction period, shortening of the chain length, and lower extent of conversion processes, etc.

In this paper we offer to use the initiated oxidation of styrene as one of the model reactions to determine the inhibitor properties of the fullerenes.

Generally the simplest scheme for the initiated oxidation of cumene at temperatures below 100°C and sufficiently high oxygen pressure [> 0.2 bar (~10⁻³ mol O₂ L⁻¹)] may be represented in the following form [13]:

Chain initiation: generation of RO₂ radicals (W₁ is initiation rate)

Chain propagation: RH + RO₂ + O₂ → ROOR'H + RO₂ (rate constant k₃)

Chain termination: 2 RO₂ → inactive products (rate constant k₆)

With RH: styrene, RO₂: styrylperoxy radical, ROOH: styrylhydroperoxide.

For the fairly long chains the reaction rate of the uninhibited reaction is described as [11]:

$$W_{O_2} = W_1^{1/2} k_3 k_6^{-1/2} [RH] = \alpha W_1^{1/2} \quad (1)$$

Where, $\alpha = k_3 k_6^{-1/2} [RH]$.

In the presence of a potential inhibitor (InH) and depending upon the mechanism of its action, the above reactions and consequently the expression (1) will be changed. As an example, in the presence of acceptors of peroxy radical the corresponding rate of the inhibited oxidation can be described by the following simplified expressions [13-15]:

$$W_{inhO_2} = W_i k_3 [RH] \{fn k_7 [InH]\}^{-1} \quad (2)$$

and

Chain initiation: generation of RO₂[•] radicals (W_i is initiation rate)

Chain propagation: $RH + RO_2^{\bullet} + O_2 \rightarrow ROOROH + RO_2^{\bullet}$ (rate constant k₃)

Chain termination: $InH + RO_2^{\bullet} \rightarrow ROOH + In^{\bullet}$ (rate constant k₇), and:

$In^{\bullet} + RO_2^{\bullet} \rightarrow$ inactive products (rate constant k₈)

Using currently accepted rate constant numeration for elementary oxidation reactions.

With : In[•] - radical of the inhibitor, W_{inhO₂} - inhibited oxidation rate, n - number of inhibiting groups in the inhibitor molecule, f- inhibition coefficient, representing the number of RO₂[•] peroxy radicals deactivated per one antioxidizing functional group of one molecule of inhibitor or the number of oxidation chains, which are terminated by one antioxidizing group of one molecule of an inhibitor (one stabilizer equivalent).

Thus, using the familiar kinetic parameters of the styrene initiated oxidation the required rate constants and inhibition coefficients can be determined.

In spite of the fact that model reactions and stabilizer reactions in polymers have much in common, the best means for final estimation of the stabilizer efficiency is its testing in the polymer under conditions of use. However, such tests often take months and even years. In order to make the time shorter the tests are accelerated. Shortening of time is reached by increasing either the temperature (in case of both thermal and oxidative degradation), or the pressure (for oxidative degradation alone).

The efficiency of stabilizers in accelerated tests can be determined by means of such physico-chemical parameters of polymer degradation as a decrease in the polymer weight and heat effect. The shifts of thermal peaks in differential thermal analysis (DTA) curves, as well as of the peaks for maximum weight loss in differential thermogravimetric analysis (TGA) curves can

be taken as quantitative characteristics of the stabilizers efficiency.

In the present work, in the first stage the model chain reaction of the initiated oxidation of styrene was used to study the antioxidative activity of fullerenes C₆₀/C₇₀ and in the second, the thermogravimetric analysis of fullerenes C₆₀/C₇₀ and C₇₀ in polystyrene was carried out.

EXPERIMENTAL

The oxidation of styrene in the presence of fullerene C₆₀/C₇₀ was conducted at the initiation rate W_i = 4.2 × 10⁻⁷ mol/L•s (AIBN)= 3.8 × 10⁻² mol/L) at 60°C and oxygen pressure P_{O₂}= 0.2 bar (air).

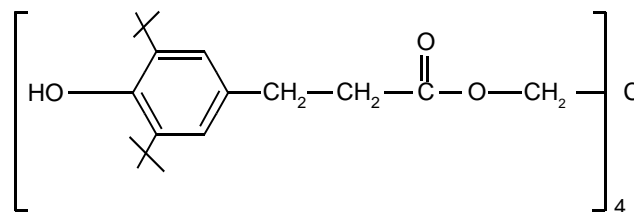
2,2'-Azo-bisisobutyronitrile (AIBN) [NC(CH₃)₂C-N-]₂ as initiator and fullerenes C₆₀/C₇₀ (85/15%) and C₇₀ by gold grade were employed .

The volume of the reaction mixture was 4 mL (25°C). The rate of oxidation was defined from the amount of oxygen consumed, which was measured manometrically [10].

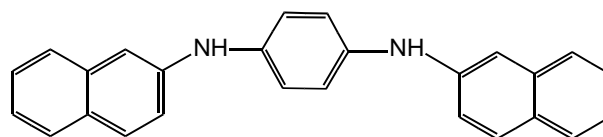
For thermogravimetric analysis the samples of polystyrene (PS) by M.W.= 5 × 10⁵ were used.

The polymer samples were mixed with fullerenes C₆₀/C₇₀ and C₇₀ and also with the well known standard antioxidants.

Irganox 1010 (Ir-1010):



and Agerite White(Ag-W) :



The samples have been studied by differential scanning calorimetry (DSC).

Measurement was done under air with a heating rate 5°C per min.

RESULTS AND DISCUSSION

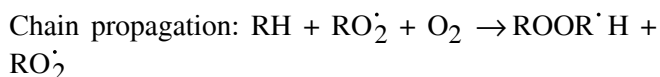
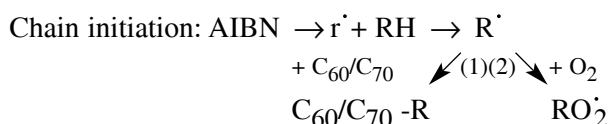
The Model Reaction

Kinetic dependencies of oxygen absorption for the initiated oxidation of styrene in the presence of fullerene C₆₀/C₇₀ are presented in Figure 1 [1-6]. It is clearly seen from the Figure 1 that with increasing of fullerene concentration the reaction rate is substantially reduced.

The inhibited oxidation proceeded without induction period and with steady rate which linearly depends on the second root of the fullerene C₆₀/C₇₀ concentration, i.e. $W_{inh(1)O_2} \sim [C_{60}/C_{70}]^{1/2}$.

Figure 2 shows the dependency between the rate of oxidation and concentration of fullerene C₆₀/C₇₀.

Based upon these obtained experimental results, the simple scheme of the styrene initiated oxidation in the presence of fullerene C₆₀/C₇₀ may be represented in the following form :



With: r' - radical of the initiator, R' - styryl radical.

The following relationships fit these mechanisms of inhibition :

$$W_{inh(1)O_2} = W_{i1}^{1/2} k_3 k_6^{-1/2} [RH] = \alpha W_{i1}^{1/2} \quad (3)$$

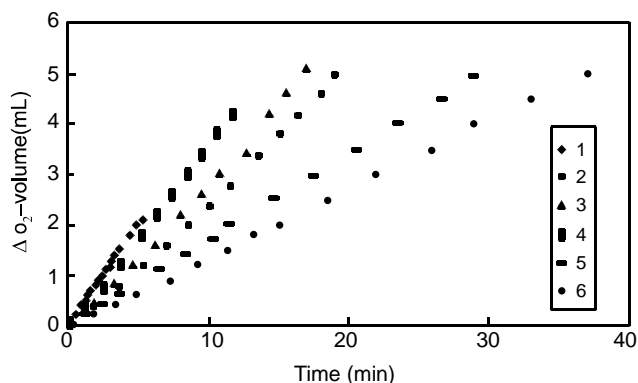


Figure 1. Initiated oxidation of styrene in the absence (1) and presence (2-6) of fullerene C₆₀/C₇₀. Reaction mixture volume 4 mL, $W_i = 4.2 \times 10^{-7}$ mol/L·s, 60°C, $P_{O_2} = 0.2$ Bar (air). $[C_{60}/C_{70}]$: (1) 0, (2) 3.0×10^{-5} , (3) 4.6×10^{-5} , (4) 6.9×10^{-5} , (5) 1.2×10^{-4} , (6) 2.3×10^{-4} mol/L.

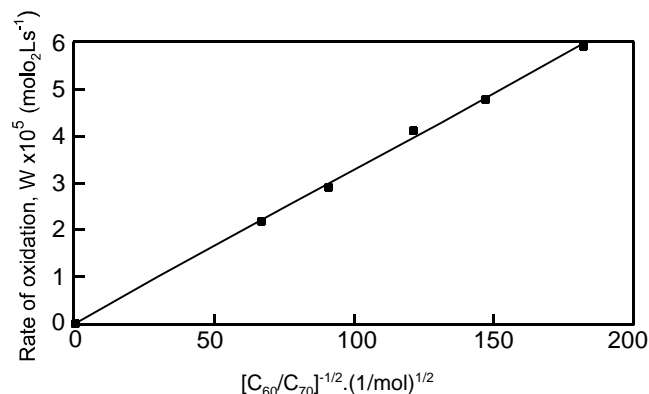


Figure 2. Rate of styrene oxidation vs fullerene C₆₀/C₇₀ concentration. Reaction mixture: volume 4 mL, $W_{i(AIBN)} = 4.2 \times 10^{-7}$ mol/L·s, 60°C.

Here: $W_{inh(1)O_2}$ and W_{i1} - rates of oxidation and initiation in the presence of fullerene C₆₀/C₇₀.

$$W_{i1} = W_i - W_1 \quad (4)$$

where, W_i - initiation rate in the absence of fullerene C₆₀ and W_1 - rate of reaction between styryl radicals and fullerene C₆₀/C₇₀ [stage(1)] equal:

$$W_1 = k_1 [R'] [C_{60}/C_{70}] \quad (5)$$

From eqn (5) the gross rate constant for addition of styryl radicals (R') to C₆₀/C₇₀ molecule can be calculated.

At steady-state conditions of oxidation in the presence of fullerene for fairly long oxidation chains the following equations are valid [12]:

$$k_2 [R'] [O_2] = k_3 [RO_2 \cdot] [RH] = W_{inh(1)O_2} \quad (6)$$

From eqns (3)-(6), using the magnitudes of the constants for styrene oxidation [11,12,16,17]:

$$k_3(333K) = 146, k_6(333K) = 3.4 \times 10^7, k_2 = 10^9, 1/\text{mol}\cdot\text{s}; [RH] = 8.26 \text{ mol/L}; [O_2] = 10^{-3}, \text{ mol/L}, \text{ one can obtain the following expressions:}$$

$$[R'] = W_{inh(1)O_2} / k_2 [O_2] = W_{inh(1)O_2} / 10^6$$

and

$$k_1 = 10^6 (W_i - W_{i1}) [C_{60}/C_{70}] W_{inh(1)O_2} = 10^6 [(W_{O_2})^2 - (W_{inh(1)O_2})^2] \alpha^{-2} \{ [C_{60}/C_{70}] W_{inh(1)O_2} \}^{-1} \quad (7)$$

The k_1 gross-value calculated for $[C_{60}/C_{70}] \leq 2.3 \times 10^{-4}$ mol/L is $k_1(333 K) = (9.0-1.5) \times 10^7$ 1/mol·s.

The obtained value of the rate constant k_1 nearly to be in accordance with the rate constants for the addition of cumyl radicals to C₆₀ obtained in our work [6]: $k(333-353K) = (2.0-0.8) \times 10^8$ 1/mol·s and also of benzyl radicals to C₆₀ determined by time-resolved ESR spectroscopy: $k(298 K) = (1.4-0.2) \times 10^7$ [4] and $k(298 K)$

Table 2. DTA Data of thermo-oxidative degradation of polystyrene (PS) without and with antioxidative additives (1%) [under air; 5°C/min., polymer's amount - 100mg].

Sample	Degradation data (°C)
PS	> 270
PS+ C ₆₀ /C ₇₀	> 305
PS+ C ₇₀	> 320
PS+ Ir-1010	> 330
PS+ Ag-W	> 340

$$= 9.3 \times 10^8 \text{ l/mol}\cdot\text{s} [5].$$

Thermo-oxidative Degradation

Polystyrene(PS) samples were dissolved in benzene and mixed with solutions of C₆₀/C₇₀ , C₇₀, Irganox-1010 (Ir-1010) and Agerite White(Ag-W) in the same solvent, respectively, each containing 1% by weight of additives/polymer. The dried polymer samples with antioxidants have been studied by differential scanning calorimetry (DSC) and thermogravimetry (TGA) .

Figure 3 represents the TGA curves for the polystyrene without and with antioxidative moieties. Data of DTA analysis is given in Table 2 .

From the data, sufficiently high stabilizing effects of C₆₀/C₇₀ and C₇₀, which are purely comparable with influence of the strongest industrial antioxidants Ir-1010 and Ag-W, are observed.

Polystyrene degradation without additives starts at

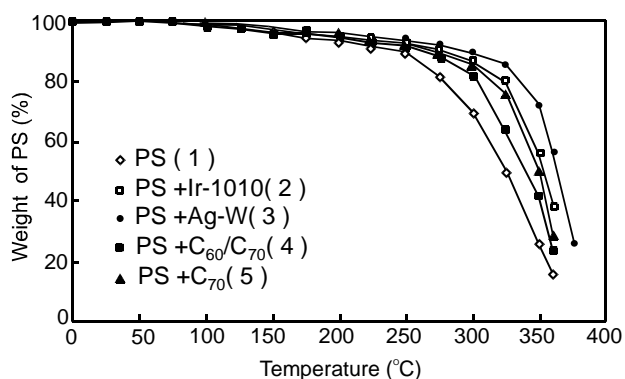


Figure 3. Thermo-oxidative degradation curves for polystyrene[PS(1)], containing 1% of additives: (2)Irganox 1010, (3)Agerite White, (4) fullerene C₆₀/C₇₀, (5)fullerene C₇₀. The polymers amount: 100 mg and heating rate: 5°C/min.

about 270°C while in the presence of 1% of fullerenes, DTA shows starting noticeable exothermic peaks at 305°C for C₆₀/C₇₀ and at 320°C for C₇₀.

Thus, the results of the accelerated tests in polystyrene confirm potential high stabilizing activity of fullerenes due to its active interaction with R' alkyl macroradicals.

CONCLUSION

According to kinetic measurements performed on a radical initiated oxidation of styrene, the antioxidative activity of fullerenes C₆₀/C₇₀ and C₇₀ has been shown. The fullerenes act as antioxidants by reacting with alkyl carbon-centred radicals. The calculated value of the rate constant of addition of the fullerene C₆₀/C₇₀ to styryl radicals is in accordance with the rate constants for the addition of benzyl and cumyl radicals to C₆₀.

The onset temperature of rapid weight loss of polystyrene in a temperature-ramped thermogravimetric experiment in air, which is 270°C for the unstabilized polymer, can be raised to 305°C and 320°C when 1% C₆₀/C₇₀ and C₇₀, respectively, are added.

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