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Antioxidant capacity of novel amine derivatives of buckminsterfullerene: Determination of inhibition rate constants in a model oxidation system

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ABSTRACT

The radical scavenging efficiency of fullerenes can be significantly activated by means of a connection with hydrogen donating groups of antioxidants such as phenolic, amine and sulfhydryl. The developed system of conjugated σ–π bonds arranged in the fullerene molecule in a closed shape can promote a strong resonance effect on the grafted units and increase the hydrogen atom abstraction efficiency. In this case the known ability of fullerene to trap alkyl radicals might be combined with the strong chain breaking functionality to afford a new class of antioxidants with bimodal action. Explorations in the field of fullerene derivatives on their antioxidant performance provide novel information on the potential stabilization properties of this type of molecular structure. A series of amine derivatives of buckminsterfullerene (C_{60}) with tethered aliphatic chain, cycloaliphatic and aromatic fragments were synthesized and their antioxidant activity was determined. The antioxidant activity of the investigated derivatives was studied by measuring the inhibition rate constants for their reaction with alkyl and peroxy radicals in a model cumene initiated (2,2′-azobisisobutyronitrile, AIBN) oxidation experiments and compared to that recorded under identical experiments for buckminsterfullerene itself and commercial primary aromatic amine stabilizers. The results indicate that linking the amine moieties groups directly to the fullerene core gives rise to a new chain breaking antioxidant mode for the buckminsterfullerene while cyclic fragments containing the same but distant amine group do not reveal this ability. The inhibition rate constants for trapping of peroxy radicals by the amine derivatives were found to be higher than that of known aromatic amine antioxidants Neozone-D and Naugard 445. In addition the C_{60} part of these molecules acts synergistically by trapping alkyl radicals with inhibition rate constants which exceed that of underivatised fullerene. The amine derivative containing sterically hindered piperidine and pyrrolidine fragments also heighten the inherent rate constant of buckminsterfullerene for scavenging alkyl radicals due to the additional antioxidant contribution promoted by the radical-quenching ability of the formed nitroxyl intermediates. These novel C_{60}–amine conjugates may be considered as promising molecules for broad-spectrum radical scavenging antioxidants.

1. Introduction

Underivatised fullerenes C_{60} and C_{70} are now widely known as effective scavengers of carbon-centred radicals [1–10]. They are recommended in practical end-use applications as inhibitors of chain radical polymerization and thermal stabilizers for polymers [2,5,6,11–27]. However, along with this advantage there are certain limits to the use of fullerenes as antioxidants because of their non-susceptibility towards peroxy radicals [2,28,29]. In order to gain information on this important reaction, essential for effective antioxidant action, fullerenes may be further modified, especially since the fullerene molecule, is essentially a fertile framework to obtain some derived molecular design with high antioxidant potency.

It is well known that the mechanism and rate of action of primary sterically hindered phenolic and aromatic amine antioxidants depends mainly on their ability to donate their phenolic or amine H-atom to a peroxyl radical. The rate of hydrogen atom abstraction is mostly governed by the positive mesomeric effect promoted by adjacent aromatic rings. Resulting phenoxy and amine-oxy radicals with their bulky substituents are stabilized by steric hindrance and cannot participate in chain propagation. Usually these radicals further recombine with other peroxy radicals or with each other, giving inert products. All mentioned factors controlling antioxidant efficiency of primary stabilizers are entirely applicable to fullerenes.

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The fullerenes have a more developed conjugated $\sigma-\pi$ bond system, larger capacity for functionalisation and a higher electron affinity than that of primary antioxidants. Thus, these peculiarities are obviously sufficiently convincing to anticipate a more pronounced antioxidant activity of fullerene derivatives with grafted hydroxyl or amine fragments. Such compounds might reveal the double antioxidant function exerted simultaneously by the fullerene moiety and a tethered functional grouping. In turn, the archetypal radical scavenging efficiency of C_{60} can be significantly altered depending on the properties and/or number of the addends on a derivatised fullerene molecule.

To date there are only a few publications in the literature regarding the antioxidant efficiency of such fullerene derivatives. Notably this concerns the polyhydroxylated fullerene $C_{60}(OH)_{24}$ in biological systems [30–33]. The fullerenol has shown excellent efficiency to scavenging stable 2,2′ –diphenyl-1-picrylhydrazyl, reactive hydroxyl (OH)–O•, nitric oxide NO• radicals, superoxide anion-radicals O_2^{-}• and other reactive oxygen species [34–39]. The hydrogen atom donation was proved by ESR detection of the fullerenol radical $C_{60}(OH)_{23}$. In addition it was established that the interaction between a hydroxyl radical and fullerenol is also based on a radical-addition reaction of $2n$ (•OH) ($n = 1$–12) radicals to the remaining olefinic bonds of a fullerenol core.

Fullerene derivatives incorporating one or two 3,5-di-tert-butyl-4-hydroxyphenyl (BHT) units were synthesized and investigated for their antioxidant activity in controlled autooxidation experiments. The results showed that grafting of the BHT structure does not qualitatively alter the thermochemistry and kinetics of its reaction with peroxy radicals but the adducts exhibit an interesting dual mode of antioxidant action [28,40].

Oil-soluble amine derivatives of buckminsterfullerene showed more antioxidant properties than zinc dialkyldithiophosphate as described in Ref. [41]. The antioxidant assay of fullerene substituted phenylaniline was determined in DMSO/PBS buffer to be significantly more potent than the alpha-tocopherol [42].

Thus, the field of antioxidant properties of fullerene derivatives may be envisioned as a new area with a promising future outlook. In this work we report the results of the determination of inhibition rate constants of a series of fullerene C_{60} amine derivatives by means of a model reaction of cumene initiated oxidation. This model oxidation has repeatedly demonstrated high resolving power on the kinetic analysis of both chain-breaking antioxidants and radical scavengers. Nowadays the model reaction serves as one of the best tools for the preliminary quantification of antioxidant efficiency and allows basically the transfer of such knowledge to a polymer system.

2. Theoretical prerequisites for the model oxidation

In our previous work we have clearly shown that the model oxidation relates to the onward assays which is effectively used for the determination of the kinetic parameters of both chain breaking antioxidants acting as acceptors of alkyl R• and/or peroxy RO_2•radicals [1,43–48]. To make the determination of kinetic parameters the model reaction of cumene initiated (initiator is 2,2′-azobisisobutyronitrile, AIBN) oxidation was designed to proceed under steady state conditions with long kinetic chains at moderate temperatures (40–80 °C) where cumylhydroperoxide does not contribute additionally to the initiation of oxidation and air oxygen pressure is sufficient not to limit the process [$Po_2 = 20$ kPa ($\approx 10^{-3}$ mol O_2 l^{-1})] [49,50].

The scheme of oxidation represented for the chain breaking antioxidants [fullerene C_{60}, hindered amine stabilizer based on 2,2′,6,6′-tetramethylpiperidine (HALS), primary phenolic or/and amine stabilizers, (InH)] has been shown to proceed according to the following mechanism:

A system of derived kinetic expressions fitting this scheme is as follows:

$$W\mathrm{o}_{2(\mathrm{C}_{60})} = k_3[\mathrm{RO_2}\bullet][\mathrm{RH}] = W_{\mathrm{i}(1)}^{1/2} k_3 k_6^{-1/2}[\mathrm{RH}] \tag{1}$$

$$W\mathrm{o}_{2(\mathrm{HALS})} = k_3[\mathrm{RO_2}\bullet][\mathrm{RH}] = W_{\mathrm{i}(1')}^{1/2} k_3 k_6^{-1/2}[\mathrm{RH}] \tag{2}$$

$$W_{\mathrm{inh}}\mathrm{o}_2 = W_{\mathrm{i(AIBN)}} k_3[\mathrm{RH}] fnk_7[\mathrm{InH}]^{-1}, \tag{3}$$

with: $W\mathrm{o}_{2(\mathrm{C}_{60})}$, $W\mathrm{o}2(\mathrm{HALS})$ and $W_{\mathrm{inh}}\mathrm{o}_2$ – rates of oxidation in the presence buckminsterfullerene, sterically hindered amine and phenolic antioxidants, respectively; $W_{\mathrm{i\,(AIBN)}}$, $W_{\mathrm{i}(1)}$, $W_{\mathrm{i}(1')}$ – initiation rates promoted by AIBN in the presence of a phenolic antioxidant, buckminsterfullerene, sterically hindered amine, respectively. n – number of functional groups in one molecule of the antioxidant; f – inhibition coefficient, representing the number of RO_2• peroxy radicals deactivated per one functional group of the antioxidant or how many oxidation chains are terminated by one antioxidant group; [InH] – concentration of the phenolic antioxidant; k_3, k_3, k_7 – rate constants of the chain propagation, termination and inhibition, respectively.

$$W_{\mathrm{i}(1)} = W_{\mathrm{i(AIBN)}} - W_{(\mathrm{C}_{60}),} \tag{4}$$

$$W_{(\mathrm{C}_{60})} = k_{(1)}[\mathrm{R}\bullet][\mathrm{C}_{60}] \tag{5}$$

is the rate of interaction between fullerene and alkyl radical.

$$W_{\mathrm{i}(1')} = W_{\mathrm{i(AIBN)}} - W_{(\mathrm{HALS})} \tag{6}$$

$$W_{(\mathrm{HALS})} = k_{(1')}[\mathrm{R}\bullet][\mathrm{HALS}(-\mathrm{NO}\bullet)] \tag{7}$$

is the rate of interaction between HALS and alkyl radical.

The oxidation inhibited by InH proceeds with an induction period, τ. The length of the induction time and inhibition rate constant k_7 are calculated according to the equations:

$$\tau = fn[\mathrm{InH}][W_{\mathrm{i(AIBN)}}]^{-1} \tag{8}$$

$$\Delta(\mathrm{O}_2)/[\mathrm{RH}] = -k_3 \ln(1 - t/\tau)/k_7 \tag{9}$$

with: t – reaction time; $\Delta(O_2)$ – volume of absorbed oxygen.

3. Experimental

3.1. Amine derivatives of buckminsterfullerene

The compounds used in this work were synthesized in the laboratory. The procedure of synthesis and their chemical structures are given in Table 1.

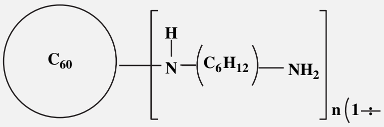
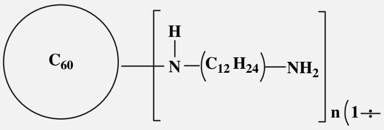
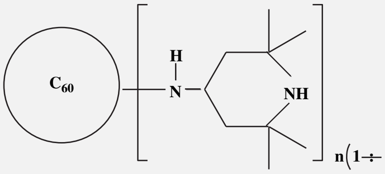
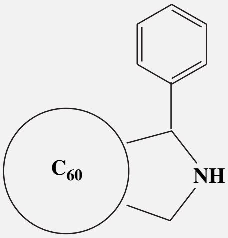
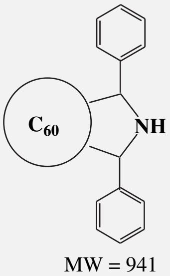
4. Characterization of the above compounds

4.1. Structures 1 + 2

1. C_{60}:H_2N–$(CH_2)_6$–NH_2
2. C_{60}:H_2N–$(CH_2)_{12}$–NH_2

Covalent bonding in the amine-C_{60} derivatives was confirmed by the UV and IR analysis. The UV spectrum of the derivative in cyclohexane shows a single descending curve with a small inflection near 260 nm, characteristic of covalent derivatives of C_{60}. There is also a shoulder present at around 420 nm due to the fullerene being present as an adduct rather than pristine [60]fullerene.

Table 1
Features of amine derivatives of buckminsterfullerene used in this work.

Symbolic notation/chemical name	Synthesis procedure	Chemical structures (molecular weight MW)
1. *C_{60} -AmAO-1*, Fullerene-hexa-methylenediamines	C_{60}:H_2N–$(CH_2)_6$–NH_2, 1:5–6 molar equivalent, stirred under N_2 at room temperature in toluene. Product washed in 40/60 petroleum ether	 MW(average) = 1065 (n = 3)
2. *C_{60} -AmAO-2*, Fullerene-dodeca-methylenediamines	C_{60}:H_2N–$(CH_2)_{12}$–NH_2, 1:5–6 molar equivalent, stirred under N_2 at room temperature in toluene. Product washed in 40/60 petroleum ether	 MW(average) = 1320 (n = 3)
3. *C_{60} -AmAO-3*, Fullerene-amino-2,2′,6,6′-tetra- methylpiperidine	C_{60}:4-amino-2,2′,6,6′-tetramethylpiperidine, 0.05 g : excess of the amine, stirred under N_2 at room temperature in toluene. Remaining amine is distilled off, product washed with hexane.	 MW(average) = 1197 (n = 3)
4. *C_{60} -AmAO-4*, Fullerene-phenyl-pyrrolidine	C_{60}:glycine:benzaldehyde, 0.07:0.14:0.35(mmol), under N_2, refluxed in toluene, purified in column chromatography	 MW = 865
5. *C_{60} -AmAO-4*, Fullerene-diphenyl pyrrolidine	C_{60}:phenylglycine:benz-aldehyde = 0.07:0.14: 0.35(mmol), under N_2, refluxed in toluene, purified in column chromatography	 MW = 941

The amine derivatives can be conditionally subdivided into three types: 1) C_{60} -AmAO-1 and C_{60} -AmAO-2 are fullerene derivatives with attached diamines of linear structure 2) C_{60} -AmAO-3 is fullerene diamine derivative containing sterically hindered piperidine moiety 3) C_{60} -AmAO-4 and C_{60} -AmAO-5 – are fullerene derivatives with grafted sterically hindered pyrrolidine fragments.

The IR spectrum contains no characteristic absorption bands of fullerene (527, 576, 1182, and 1428 cm^{-1}), and most importantly the signal seen when a fullerene–monoadduct is present, at 527 cm^{-1}, is clearly absent in this case, which leads us to believe that a polyadduct has been synthesized. The appearance of intense bands at 1000–1200 cm^{-1} (vibrations of the C–N bond) and strong bands around 2950 cm^{-1} (arising from the C–H stretching vibrations of the aliphatic portions of the molecule) confirm the covalent addition of 1,6-diaminohexane/1,12-diaminododecane to C_{60}. Vibrations characteristic of an NH_2 group (3336 cm^{-1}) can still be seen therefore suggesting covalent bonding between the amine and fullerene has taken place at only one of the possible two amine sites within the diamine molecule.

^{13}C NMR was carried out on these two compounds. For polyadditions a broad maximum at 140–150 ppm would replace the narrow peak at 143 ppm seen in pure C_{60} (monoadducts are represented by a set of well resolved lines in the 140–150 ppm region). Signals at 67–72 ppm, characteristic of sp^3 atoms of the modified fullerene, should be seen upon addition of amines at the fullerenes double bonds, these were also absent. Peaks should also have been seen in the alkyl region 15–35 ppm for the hexane backbone of the diamine, these were also absent.

MS was complex due to 1–6 additions on the fullerene structure.

4.2. Structure 3

C_{60}:4-amino-2,2′,6,6′-tetramethylpiperidine

Covalent bonding in the amine-C_{60} derivatives was confirmed by the UV and IR analysis. The UV spectrum of the derivative in cyclohexane shows a single descending curve with a small inflection near 260 nm, characteristic of covalent derivatives of C_{60}. There is also a shoulder present at around 420 nm due to the fullerene being present as an adduct rather than pristine [60]fullerene.

The IR spectrum, carried out as a KBr disk, contains no absorption bands characteristic of pristine C_{60} (527, 576, 1182, and 1428 cm^{-1}) which implies a polyadduct has been synthesized. The signal seen when a C_{60} monoadduct is present, 527 cm^{-1}, is clearly absent thus supporting the idea of a polyadduct being synthesized. The appearance of bands at 1000–1200 cm^{-1} (vibrations of the C–N bond) and strong bands around 2964 cm^{-1} (arising from the C–H stretching vibrations of the aliphatic portions of the molecule) confirm the covalent addition of 4-amino-2,2,6,6-tertramethylpiperidine to C_{60}. A single peak characteristic of an NH group (3300 cm^{-1}) can be seen therefore, suggesting covalent bonding between the amine and fullerene has taken place at the primary amine thus leaving two secondary amines in the final product.

^{13}C NMR was carried out on the compound. For polyadditions a broad maximum at 140–150 ppm would replace the narrow peak at 143 ppm seen in pure C_{60} (monoadducts are represented by a set of well resolved lines in the 140–150 ppm region). Signals at 67–72 ppm, characteristic of sp3 atoms of the modified fullerene, should be seen upon addition of amines at the fullerenes double bonds, these were also absent. Peaks should also have been seen in the alkyl region 15–35 ppm for the hexane backbone of the diamine, these were also absent.

Again MS was not suitable for these materials.

4.3. Structure 4

C_{60}:glycine:benzaldehyde

The infrared spectrum shows a single peak around 3300 cm^{-1} which indicates the presence of a secondary amine group, with C–H stretching vibrations for the aromatic and aliphatic (–CH and –CH_2) parts of the pyrrolidine ring seen at 3020, 2921 and 2850 cm^{-1} respectively. The skeleton absorptions of [60]fullerene have changed, however the peak at 527 cm^{-1} is clearly present showing that the fullerene cage is intact and that no additional groups have bonded to the cage and a monoadduct has been synthesized.

The UV spectrum of the derivative in cyclohexane shows a single descending curve with a small inflection near 260 nm, characteristic of covalent derivatives of C_{60}. There is also a shoulder present at around 420 nm due to the fullerene being present as an adduct rather than pristine [60]fullerene.

The ^{13}C NMR spectrum exhibits a set of well resolved lines in the 140–150 ppm region typical of a monoadduct, where the initial fullerene has a narrow peak at 143 ppm and polyadducts exhibiting a broad maximum at 140–150 ppm. The signals at 63–72 ppm, characteristic of sp^3 atoms of the modified fullerene, appear upon addition of amines at double bonds of the fullerene. Signals at 29 and 30 ppm are attributed to the carbon atoms of the CH_3 and CH_2 groups in the piperidine ring.

Analysis by MALDI mass spectrometry gave a peak at m/z 839 which corresponds to the molecular ion with a peak at m/z 720 which is the M+ for [60]fullerene.

4.4. Structure 5

C_{60}:phenylglycine:benzaldehyde

Infrared via KBr disc, showed a single prominent peak at 3320 cm^{-1} indicating the presence of a secondary amine, C–H stretching vibrations attributed to the aromatic and aliphatic (–CH) portions of the pyrrolidine ring can be seen at 3028, 2901 and 2850 cm^{-1} respectively. As expected for the presence of a monoadduct, the skeleton absorptions which are seen for pristine [60]fullerene at 1428, 1183, 577 and 527 cm^{-1}, have changed, with the only peak remaining unchanged being observed at 527 cm^{-1}, showing that the fullerene cage is intact, no additional groups have bonded to the cage, and a monoadduct has been synthesized.

Comparisons between the UV–Vis spectra of pristine [60]fullerene and 2,5-diphenylpyrrolidino[60]fullerene shows almost identical spectra, with 2,5-diphenylpyrrolidino[60]fullerene exhibiting an additional characteristic peak around 430 nm which is attributed to the presence of a 6,6-closed monoadduct.

The ^{13}C NMR spectrum exhibits a set of well resolved lines in the 140–150 ppm region typical of a monoadduct, where the initial fullerene has a narrow peak at 143 ppm and polyadducts exhibiting a broad maximum at 140–150 ppm. The signals at 63–75 ppm, characteristic of sp^3 atoms of the modified fullerene, appear upon addition of amines to the double bonds of fullerene. Signals at 21, and 27 ppm are attributed to the carbon atoms of the CH_3 and CH_2 groups in the piperidine ring.

Analysis by MALDI mass spectrometry gave rise to a peak at m/z 915 which corresponds to the molecular ion with a peak at m/z 720 which is the M+ for [60]fullerene.

4.5. Model reaction of cumene oxidation

To study the chain breaking antioxidants the model cumene oxidation was undertaken at initiation rates: $W_i = 1.7 \times 10^{-8} - 6.8 \times 10^{-8}$ M s^{-1}, temperatures: 60 and 80 ($\pm$0.02)°C and oxygen pressure:$Po_2 = 20$ kPa (air). The employed cumene was 98% purity («Aldrich»).

2,2′-azobisisobutyronitrile (AIBN) was used as the initiator. The volume of the reaction mixture was 10 cm^3 (25 °C). To achieve the assigned initiation rates 0.72–10 mg (at 60–80 °C) of AIBN had to be added [49–51].

The rate constants of chain propagation and termination for the cumene oxidation at 60 and 80 °C have the following values: $k_3 = 1.75$ and 4.05; $k_6 = 1.84 \times 10^5$ and 3.08×10^5 M^{-1} s^{-1}, respectively; concentration of cumene [RH] = 6.9 (60 °C) and 6.76 (80 °C) mol l^{-1}. The rates of oxidation were evaluated by considering the amount of oxygen consumed, which was measured volumetrically with the simple equipment as described in [43,50]. Oxidation rates were assessed both from slopes of the kinetic curves of oxygen consumption in the case of steady rate values and also by means of differentiating the curve in the case of an observed induction period.

Induction periods were graphically evaluated from kinetic curves [49,50].

Values of the inhibition rate constant k_7 were found from the slopes of semilogarithmic transformation of oxygen absorption curves according to the relationship.

$$k_7 = 2.3\,k_3[\mathrm{RH}](\mathrm{tg}\alpha)^{-1} \tag{10}$$

with $\mathrm{tg}\alpha = \Delta(\mathrm{O}_2)\,[-\mathrm{lg}\,(1 - t/\tau)]^{-1}$

From the experimentally observed values of oxidation rates, using the known rate constants for cumene oxidation it is possible to determine inhibition rate constants k_1 (or $k_{1'}$) for the trapping cumylalkyl radicals by the fullerene or HALS type compounds:

$$k_1[\mathrm{R}^\bullet][\mathrm{C}_{60}]k_{1'}[\mathrm{R}^\bullet][\mathrm{HALS}] = W_{\mathrm{i(AIBN)}} - [W\mathrm{o}_{2(\mathrm{C}_{60})}]^2 W\mathrm{o}_{2(\mathrm{HALS})}k_6(k_3)^{-2}[\mathrm{RH}]^{-2} \tag{11}$$

Experiments were carried out at least in triplicate and the correctness in determining the kinetic parameters was within the range 1–10%.

5. Results and discussion

5.1. Kinetic study of C_{60} -AmAO-1 and C_{60} -AmAO-2

The compounds are similar to the aromatic amines with alkyl substituents which are usually well-amenable to the kinetic analysis by means of the model oxidation [6,48,49]. The profiles of kinetic dependencies of oxygen uptake for the system cumene + AIBN + C_{60} -AmAO-1 and C_{60} -AmAO-2 are exemplified in Fig. 1. As the compounds did not dissolve in cumene, their fine suspension was used in the analysis.

Thus the C_{60} -AmAO-1 and C_{60} -AmAO-2 retard the oxidation of cumene, exhibiting distinct induction periods and post-induction oxidation rates which are however, markedly lower than the dependences without additives (1, 3, 5, shown in Fig. 1). The induction periods reflect the action of the secondary amine group directly connected to the fullerene core while the underivatised fullerene is responsible for the lowered post-induction oxidation rates. Kinetic curves show that the action of the amine derivatives is consistent with the above-mentioned scheme.

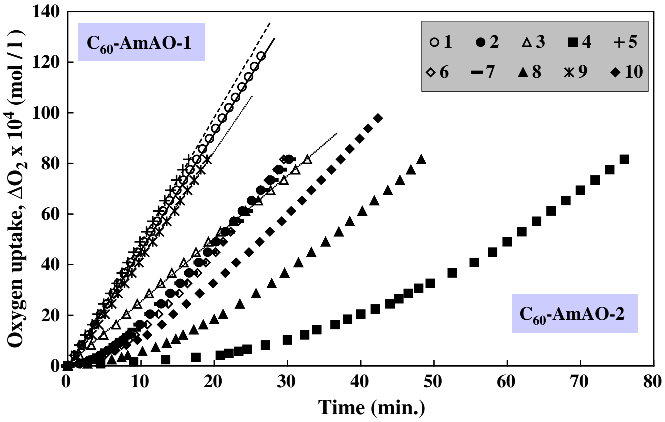


Fig. 1. Kinetic dependencies of oxygen uptake for cumene initiated oxidation in the presence of C_{60} -AmAO-1 and C_{60} -AmAO-2. Initiator is 2,2′-azobisisobutyronitrile (AIBN). Reaction mixture volume 10 ml, amounts of C_{60} -AmAO-1 and C_{60} -AmAO-2 = 10 mg each, oxygen pressure:$P\mathrm{o}_2$ = 20 kPa (air), 60° and 80 °C. C_{60} -AmAO-1 = 10 mg: 60 °C – (**1**) 0 ($W_i = 6.8 \times 10^{-8}$ M s^{-1}); (**2**) + $W_i = 6.8 \times 10^{-8}$ M s^{-1}; (**3**) 0 ($W_i = 1.7 \times 10^{-8}$ M s^{-1}); (**4**) + $W_i = 1.7 \times 10^{-8}$ M s^{-1}; 80 °C – (**5**) 0 ($W_i = 2.7 \times 10^{-8}$ M s^{-1}); (**6**) + $W_i = 2.7 \times 10^{-8}$ M s^{-1}; C_{60} -AmAO-2 = 10 mg: 60 °C – (**7**) + $W_i = 6.8 \times 10^{-8}$ M s^{-1}; (**8**) + $W_i = 1.7 \times 10^{-8}$ M s^{-1}; 80 °C – (**9**) 0 ($W_i = 2.0 \times 10^{-8}$ M s^{-1}); (**10**) + $W_i = 2.0 \times 10^{-8}$ M s^{-1}.

In order to determine the inhibition rate constants for the functional amine groups of C_{60} -AmAO-1 and C_{60} -AmAO-2 semilogarithmic transformations of the initial plots of kinetic curves 4, 6, 8 and 10 (Fig. 1) are plotted in Fig. 2.

Inhibition rate constants obtained from the transformations processed and calculated according to Eq. (10) are represented in Table 2.

Thus, the values of inhibition rate constants for interaction of the amine derivatives of buckminsterfullerene with peroxy radicals shown in Table 1 rather exceed the same constants for the known commercial primary antioxidants. In the amine derivatives the unshared pair of electrons is delocalized along the system of the fullerene π-bonds. The nitrogen atom in the system operates as a donor of electrons and the amine group exhibits a positive mesomeric effect (M^+) which totally suppresses the negative inductive effect (I^-).

5.2. Kinetic analysis of C_{60} -AmAO-3

This amine derivative has an interesting structure where the sterically hindered piperidine unit which is widely known as a precursor of nitroxyl radicals is connected with secondary amine groups directly grafted to the buckminsterfullerene core. Hence, the mentioned double antioxidant capacity of the molecule due to hydrogen atom abstraction of the –NH group followed by interaction with peroxy radicals and additionally scavenging of alkyl radicals by nitroxyl radicals and the fullerene part itself might be expected.

The kinetic regularities of oxygen consumption, dependence of induction period vs C_{60} -AmAO-3 content as well as semilogarithmic patterns of the initial plots of kinetic curves are shown in Figs. 3 and 4, respectively.

The results of the inhibition rate constant k_7 determination for the compound C_{60} -AmAO-3 are given in Table 2. It may be seen that the value is practically similar to those found for C_{60} -AmAO-1 and C_{60} -AmAO-2.

The values of post-induction oxidation rates of the kinetic curves plotted in Fig. 3 are lower than that of benchmark dependency (curve1). The lowering has occurred because of the simultaneous trapping of alkyl radicals by the fullerene part of the

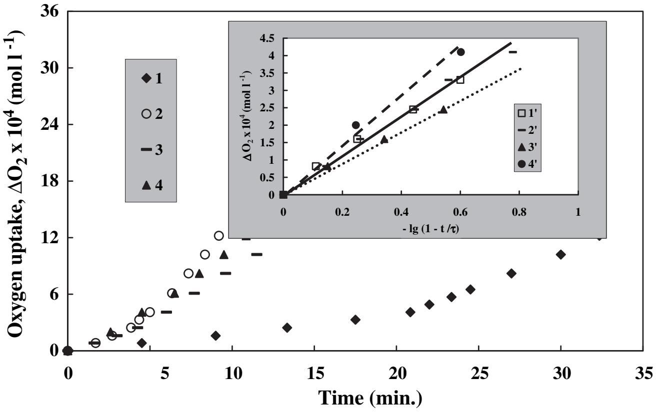


Fig. 2. Semilogarithmic transformations of the initial plots of kinetic curves of oxygen consumption for cumene initiated oxidation in the presence of C_{60} fullerene amine derivatives. Reaction mixture volume 10 ml, oxygen pressure:$P\mathrm{o}_2$ = 20 kPa (air), 60° and 80 °C. C_{60} -AmAO-1 = 10 mg : 60 °C – (**1**) + $W_i = 1.7 \times 10^{-8}$ M s^{-1} and corresponding transformation (**1′**); 80 °C – (**2**) + $W_i = 2.7 \times 10^{-8}$ M s^{-1} with transformation (**2′**). C_{60} -AmAO-2 = 30 mg : 60 °C – (**3**) + $W_i = 1.7 \times 10^{-8}$ M s^{-1}; C_{60} -AmAO-2 = 10 mg: 80 °C – (**4**) + $W_i = 2.0 \times 10^{-8}$ M s^{-1} and their transformations (**3′**) and (**4′**), respectively.

Table 2

Kinetic parameters of antioxidant activity of the amine derivatives of buckminsterfullerene C_{60} -AmAO-1 and C_{60} -AmAO-2 and known primary antioxidants in the model reaction of cumene initiated oxidation. Amount of C_{60} -AmAO-1/2 = 10 mg, $W_i = (1.7–2.7) \times 10^{-8}$ M s^{-1}, oxygen pressure Po_2 = 20 kPa (air), 60° and 80 °C. $(k_7)_0$ – pre-exponential factor, E – activation energy.

Antioxidant	lg $(k_7)_{(333K)}$ (M^{-1} s^{-1})	lg $(k_7)_{(353K)}$ (M^{-1} s^{-1})	lg $(k_7)_0$	E/kJ mol^{-1}
C_{60} -AmAO-1	4.95 ± 0.01	5.08 ± 0.01	7.25 ± 0.32	14.7 ± 2.1
C_{60} -AmAO-2	4.96 ± 0.01	5.04 ± 0.01	6.40 ± 0.33	9.2 ± 2.1
C_{60} -AmAO-3	4.95 ± 0.01	5.04 ± 0.01	6.50 ± 0.40	10.1 ± 2.5
Naugard 445, 4,4′-Bis(α,α-dimethylbenzyl) diphenylamine	4.91 ± 0.02	5.0 ± 0.01	6.50 ± 0.50	10.1 ± 3.4 [48]
Neozone-D, Phenyl–2-naphthylamine	4.83 ± 0.03	4.96 ± 0.02	7.03 ± 0.39	14.2 ± 5.9 [49]

molecule C_{60} -AmAO-3 and by the 2,2′,6,6′-tetramethylpiperidine moiety of the substituent. In order to quantify the inhibition rate constant of alkyl radical scavenging the post-induction time plots of kinetic curves of oxygen consumption were arranged in Fig. 5 and calculated oxidation rates were compared with that obtained for the fullerene C_{60} molecule only [1].

In our earlier work [43] it was shown that the model cumene oxidation allows correct determination of antioxidants behaving as peroxy and alkyl radical scavengers simultaneously. On this basis the determination might be applicable for blends of primary antioxidants and alkyl radical scavengers, and also for one molecule which constitutes both functionalities. The presence of primary antioxidants did not counteract the determination of the alkyl radical scavengers and vice versa.

The data shown in Fig. 5 shows quite a good proportionality between the experimentally observed values of oxidation rates $Wo2(C_{60})$–$Wo2(C_{60}$ -AmAO-3) and the square root of concentration (C) of the compounds i.e. $Wo2(C_{60}) - Wo2(C_{60\text{ -AmAO-3}} \sim [C]^{1/2}$. This implies that the buckminsterfullerene and its amine derivative C_{60} -AmAO-3 actively intercept the alkyl radicals and decrease the rate of initiation and accordingly the rate of oxidation. In this case the following expressions similar to Eqs. (1), (2), ((4)–(7)) for the oxidation, initiation and rate of C_{60} -AmAO-3 interaction with alkyl radicals are valid:

$$Wo_{2(C_{60}-\text{AmAO}-3)} = k_3[\text{RO}_2\bullet][\text{RH}] = W^{1/2}_{i(C_{60}-\text{AmAO}-3)}k_3k_6^{-1/2}[\text{RH}] \tag{12}$$

$$W_{i(C_{60}-\text{AmAO}-3)} = W_{i(\text{AIBN})} - W_{(C_{60}-\text{AmAO}-3)} \tag{13}$$

$$W_{(C_{60}-\text{AmAO}-3)} = k_{(C_{60}-\text{AmAO}-3)}[\text{R}\bullet][C_{60}-\text{AmAO}-3] \tag{14}$$

Using the experimentally observed values of oxidation rates and known rate constants for cumene oxidation we may determine Wi (C_{60} -AmAO-3) from Eq. (12) and afterwards from equation Eqs. (13) and (14) an inhibition rate constant k(C_{60}-AmAO-3) for the trapping of cumylalkyl radicals by the buckminsterfullerene amine derivative:

$$\begin{aligned} &k_{(C_{60}-\text{AmAO}-3)}[\text{R}\bullet][C_{60}-\text{AmAO}-3] \\ &\quad = W_{i(\text{AIBN})} - [Wo_{2(C_{60}-\text{AmAO}-3}]^2 k_6 (k_3)^{-2}[\text{RH}]^{-2} \end{aligned} \tag{15}$$

At steady state conditions of the oxidation for fairly long chains the rate of oxidation may be represented as [52,53]:

$$k_2[\text{R}\bullet][\text{O}_2] = k_3[\text{RO}_2\bullet][\text{RH}] = Wo_{2(C_{60}-\text{AmAO}-3)} \tag{16}$$

Using the known magnitudes of constants for cumene oxidation (see Experimental section) and assuming $k_2 = 10^9$ M^{-1} s^{-1} and $[\text{O}_2] = 10^{-3}$ M [52–55] the following expressions can be obtained for calculation of $k_{(C_{60}}$-AmAO-3):

$$\begin{aligned} &[\text{R}\bullet] = Wo_{2(C_{60}-\text{AmAO}-3)}/k_2[\text{O}_2] = Wo_{2(C_{60}-\text{AmAO}-3)}/10^6, \\ &\quad k_{(C_{60}-\text{AmAO}-3)} = 10^6 W_{i(\text{AIBN}0} - [Wo_{2(C_{60}-\text{AmAO}-3}]^2 k_6(k_3)^{-2} \\ &\quad [\text{RH}]^{-2}[C_{60}-\text{AmAO}-3]^{-1}[Wo_{2(C_{60}-\text{AmAO}-3}]^{-1} \end{aligned} \tag{17}$$

Rate constant value for the C_{60} -AmAO-3 calculated from Eq. (17) over the concentration range 1×10^{-5}–5×10^{-5} mol/l and also that for known antioxidants acting as alkyl radical acceptors are collected in Table 3.

5.3. Kinetic analysis of C_{60} -AmAO-4 and C_{60} -AmAO-5

The compound structures are composed of a directly grafted buckminsterfullerene with pyrrolidine fragments having sterically hindered bulky phenyl substituents. Apparently such a propriety

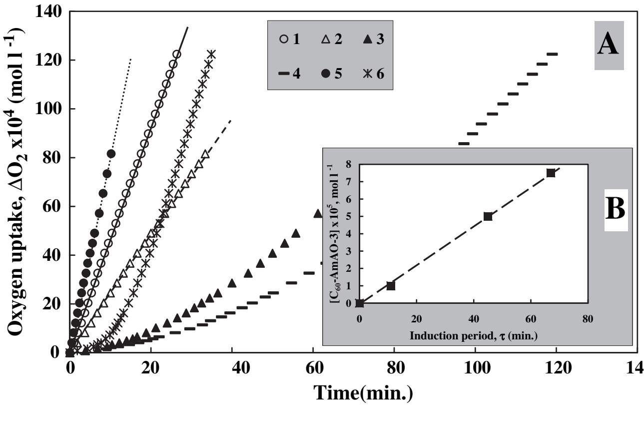


Fig. 3. Kinetic dependencies of oxygen uptake (A) and dependence induction period vs content (B) for cumene initiated oxidation in the presence of buckminsterfullerene amine derivative C_{60} -AmAO-3. Initiator is 2,2′-azobisisobutyronitrile (AIBN), initiation rate: $W_i = 6.8 \times 10^{-8}$ M s^{-1}, reaction mixture volume:10 ml, oxygen pressure:Po_2 = 20 kPa (air), 60° and 80 °C. A – [C_{60} -AmAO-3]: 60 °C – (**1**) 0; (**2**) 1.0×10^{-5}; (**3**) 5×10^{-5}; (**4**) 7.5×10^{-5}, mol l^{-1} 80 °C – (**5**) 0; (**6**) $2. \times 10^{-5}$, mol l^{-1}.

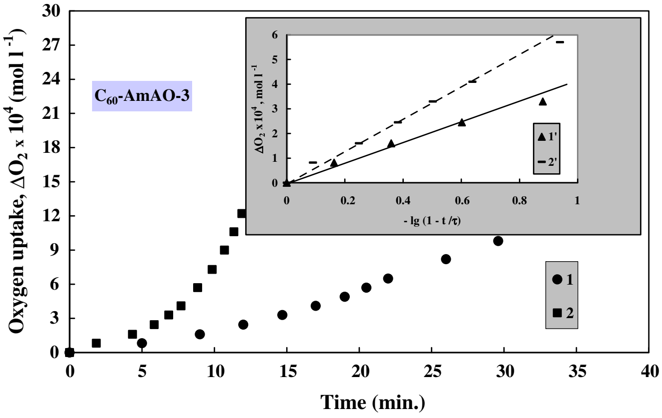


Fig. 4. Initial plots of kinetic curves of oxygen uptake (1, 2) and their graphical transformations (1′, 2′) for cumene initiated oxidation in the presence of buckminsterfullerene amine C_{60} -AmAO-3. Reaction mixture volume:10 ml, rate of initiation: $W_{i(AIBN)} = 6.8 \times 10^{-8}$ M s^{-1}, oxygen pressure:Po_2 = 20 kPa (air). 1: [C_{60} -AmAO-3] = 7.5×10^{-5} mol/l, 60 °C; 2: [C_{60} -AmAO-3] = 2.0×10^{-5} mol/l, 80 °C.

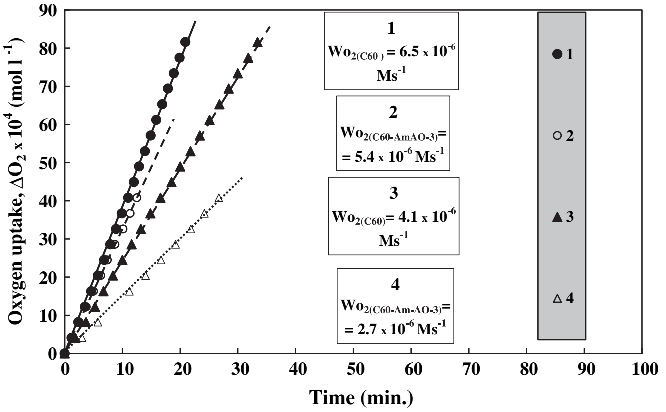


Fig. 5. Kinetic lines of oxygen oxygen-uptake during aerobic initiated oxidation of cumene in the presence of buckminsterfullerene (1, 3) and the amine derivative C_{60} -AmAO-3 (2, 4; post-induction period plots are given). The initiator is 2,2′-azobisisobutyronitrile (AIBN), initiation rate:$W_i = 6.8 \times 10^{-8}$ mol/l s, reaction mixture volume 10 ml, oxygen pressure:$Po_2 = 20$ kPa (air), temperature: 60 °C. [C_{60}] and [C_{60} -AmAO-3]: $(1, 2) = 1 \times 10^{-5}$, $(3, 4) = 5 \times 10^{-5}$ mol/l.

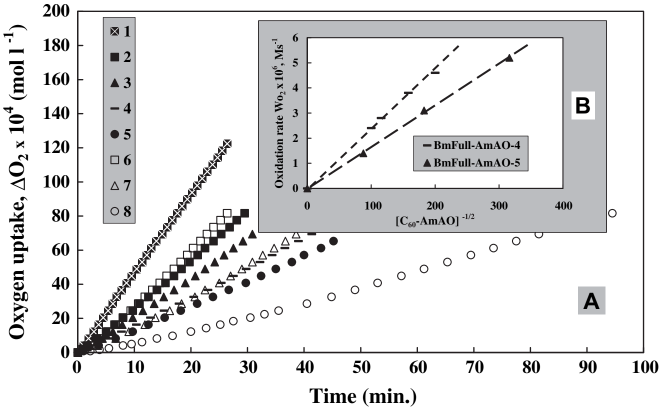


Fig. 6. Kinetic dependences of oxygen oxygen-uptake (A) for initiated oxidation of cumene in the absence (1) and presence of different amounts of amine derivatives of fullerene C_{60} (2–8); B: is plot of induction period versus concentration of the compounds. The initiator is 2,2′-azobisisobutyronitrile (AIBN), initiation rate:$W_i = 6.8 \times 10^{-8}$ M s^{-1}, reaction mixture volume:10 ml, oxygen pressure:$Po_2 = 20$ kPa (air), temperature: 60 °C. Concentration of the fullerene derivatives – [C_{60} -AmAO-4]:(**1**) = 0, (**2**) = 2.5×10^{-5}, (**3**) = 4×10^{-5}, (**4**) = 7.5×10^{-5}, (**5**) = 1.0×10^{-4}, mol/l; [C_{60} -AmAO-5]: (**1**) = 0, (**6**) = 1.0×10^{-5}, (**7**) = 3×10^{-5}, (**8**) = 1.3×10^{-4}, mol/l.

head to tail structure is a good realization for the mechanism of alkyl radical scavenging. Fig. 6 represents the kinetic dependences of oxygen uptake in the model oxidation reaction in the presence of C_{60} -AmAO-4 and C_{60} -AmAO-5.

It is seen from Fig. 6 that over a sufficient wide range of concentrations of added amine derivatives the kinetic curves of oxygen consumption do not exhibit any induction period and the model oxidation proceeds with a retarded steady oxidation rate. Such a behaviour pattern is consistent with Scheme 1 and the related Eqs.(1), (2), (12). The dependence plotted in Fig. 5(B) manifests quite a good linearity between the experimentally observed oxidation rates.

Wo_2 (C_{60} $_{\text{-AmAO-4/5)}}$ and the square root of the concentration of the compounds over the range 1×10^{-5}–1.3×10^{-4} mol/l i.e. $Wo_2(C_{60\ \text{-AmAO-4/5}}) - [C_{60}\ \text{-AmAO-4/5}]^{1/2}$.

The inhibition rate constants for the C_{60} -AmAO-4 and C_{60} -AmAO-5 may be calculated in the same way as for the C_{60} -AmAO-3 from Eq. (18):

$$k_{(C_{60}-\text{AmAO}-4/5)} = 10^6 W_{i(\text{AIBN0}} - [Wo_{2(C_{60}-\text{AmAO}-4/5)}]^2 k_6 (k_3)^{-2} [\text{RH}]^{-2} [C_{60} - \text{AmAO} - 4/5]^{-1} [Wo_{2(C_{60}-\text{AmAO}-4/5)}]^{-1} \quad (18)$$

Values of the inhibition rate constants found for the buckminsterfullerene amine derivatives C_{60} -AmAO-4 and C_{60} -AmAO-5 over the concentration range 1×10^{-5}–1.3×10^{-4} mol/l are given in Table 3.

The evaluated rate constants appear to be considerably higher than those of fullerene and the commercials stabilizers, confirming the existence of a synergistic effect promoted by the fullerene component and the tethered amine units. It is possible also to infer that the more the steric hindrance in the grafted cyclic amines the higher are the values of inhibition rate constants.

6. Conclusions

The results obtained in this work provide evidence that the buckminsterfullerene derivatives containing grafted antioxidant units exhibit higher efficiency than conventional antioxidants. The fullerene system of conjugated σ–π bonds gives rise to a strong resonance effect with grafted phenolic or amine groups and facilitates an instantaneous detachment of a hydrogen atom to exert a strong antioxidant effect in the modified fullerene molecule. The ready abstraction of a hydrogen atom from the functional groups coupled with the high intrinsic radical scavenging efficiency of the buckminsterfullerene is supportive of a dual mode of antioxidant action. The values of inhibition rate constants found also corroborate the fact that the grafted sterically hindered piperidine moieties are able to iteratively increase the inherent radical scavenging efficiency of the fullerene.

Table 3
Rate constants for the addition of cumylalkyl radicals to the buckminsterfullerene, amine derivatives of buckminsterfullerene and some alkyl radical accepting stabilizers.

Antioxidant/stabilizer	The inhibition rate constant, $k_{(333K)}$ M^{-1} s^{-1}	Reference
C_{60}	$(1.9 \pm 0.2) \times 10^8$	[1]
C_{60} -AmAO-3	$(5.1 \pm 0.6) \times 10^8$	Found
C_{60} -AmAO-4	$(3.1 \pm 0.5) \times 10^8$	Found
C_{60} -AmAO-5	$(5.4 \pm 0.8) \times 10^8$	Found
Cyasorb 3529, (1,6-Hexanediamine, N,N′-bis (2,2,6,6-tetramethyl-4-piperidinyl)-, Polymers with morpholine-2,4,6,-trichloro-1,3,5,- triazine)	$(2.0 \pm 0.8) \times 10^8$	[46]
Chimassorb 119, (1,3,5-Triazine-2,4,6,-triamine,N,N‴-[1,2-ethane-diyl-bis [[[4,6-bis-[butyl (1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2yl-]imino]-3,1-propanediyl]]bis [N′,N″-dibutyl-N′, N″-bis (1,2,2,6,6-pentamethyl-4-piperidinyl)	$(1.2 \pm 0.2) \times 10^8$	[45]
Chimassorb 119FL	$(1.4 \pm 0.2) \times 10^8$	[45]
Chimassorb 2020, (1,6-Hexanediamine, N, N′-bis(2,2,6,6-tetramethyl-4-piperidinyl)-polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-1-butanamine an N-butyl-2,2,6,6-tetramethyl-4-piperidinamine)	$(1.5 \pm 0.2) \times 10^7$	[43]

Chain initiation : $\mathbf{AIBN} \rightarrow \mathbf{r}^{\cdot}\ (\mathbf{rO_2}^{\cdot}) + \mathbf{RH} \rightarrow \mathbf{R}^{\cdot}$ (initiation rate is $\mathbf{W_i}$)

$$\mathbf{R}^{\cdot} + \mathbf{C_{60}} \rightarrow {}^{\cdot}\mathbf{C_{60}\ R} \text{ (rate constant } \mathbf{k_1}\text{)} \qquad \mathbf{(1)}$$

$$\mathbf{R_1\text{-}NH} \rightarrow \mathbf{R_1\text{-}NO}^{\cdot} + \mathbf{R}^{\bullet} \rightarrow \mathbf{R_1\ \text{-}NOR} + \text{ inert products (rate constant } \mathbf{k_{1'}}\text{)} \qquad \mathbf{(1')}$$

Chain propagation: $\mathbf{R}^{\cdot} + \mathbf{O_2} \rightarrow \mathbf{RO_2}^{\cdot} + \mathbf{RH} \rightarrow \mathbf{ROOH} + \mathbf{R}^{\cdot}$ (rate constant $\mathbf{k_2/k_3}$) **(2)/(3)**

Chain termination: $\mathbf{2\ RO_2}^{\cdot} \rightarrow$ inactive products (rate constant $\mathbf{k_6}$) **(6)**

$$\mathbf{RO_2}^{\cdot} + \mathbf{InH} \rightarrow \mathbf{ROOH} + \mathbf{In}^{\cdot} \text{ (rate constant } \mathbf{k_7}\text{)} \qquad \mathbf{[7]}$$

$$\mathbf{RO_2}^{\cdot} + \mathbf{In}^{\cdot} \rightarrow \text{ inactive products (rate constant } \mathbf{k_8}\text{)} \qquad \mathbf{[8]}$$

$$\mathbf{In}^{\cdot} + \mathbf{In}^{\cdot} \rightarrow \text{ inactive products (rate constant } \mathbf{k_9}\text{)} \qquad \mathbf{[9]}$$

where : **RH**: cumene, $\mathbf{R}^{\bullet}$: cumylalkyl radical, $\mathbf{RO_2}^{\bullet}$: cumylperoxy radical, **ROOH** : cumylhydroperoxide) , $\mathbf{C_{60}}$: buckminsterfullerene, ${}^{\cdot}\mathbf{C_{60}\ R}$: radical adduct of buckminsterfullerene; $\mathbf{R_1\text{-}NH}$: hindered amine stabilizer (HALS) $\mathbf{R_1\text{-}NO}^{\bullet}$: nitroxyl radical; **InH** : primary phenolic or amine antioxidant; $\mathbf{In}^{\cdot}$: radical of the antioxidant;

* Here the generally accepted oxidation stage numbering is used.

Scheme 1. *General scheme of the model cumene initiated oxidation in the presence of chain-breaking antioxidants.

Thus the fullerene derivatives may be recognized as a new promising class of antioxidants. However, many challenges remain and, the inference requires further thorough explorations.

References

[1] Zeynalov EB, Allen NS, Salmanova NI. Radical scavenging efficiency of different fullerenes C_{60}–C_{70} and fullerene soot. Polymer Degradation and Stability 2009;94(8):1183–9.

[2] Zeynalov EB, Friedrich JF. Anti-radical activity of fullerenes and carbon nanotubes in reactions of radical polymerization and polymer thermal/thermooxidative degradation-a review. Materials testing (Materials and Components, Technology and Application) section. Polymer Materials 2007;49(5):265–70.

[3] Guldi DM, Hungerbuhler H, Janata E, Asmus KD. Radical- induced redox and addition-rections with C-60 studied by pulse-radiolysis. Journal of the Chemical Society-Chemical Communications 1993;1:84–6.

[4] Dimitrijevic NM, Kamat PV, Fessenden RW. Radical adducts of fullerenes C-60 and C-70 studied by laser flash-photolysis and pulse-radiolysis. Journal of Physical Chemistry 1993;97(3):615–8.

[5] Zeinalov EB, Koβmehl G. Fullerene C_{60} as an antioxidant for polymers. Polymer Degradation and Stability 2001;71(2):197–202.

[6] Zeynalov EB, Magerramova MY, Ischenko NY. Fullerenes C-60/C-70 and C-70 as antioxidants for polystyrene. Iranian Polymer Journal 2004;13(2):143–8.

[7] Gasanov RG, Kalina OG, Bashilov VV, Tumanskii BL. Addition of carbon-centered radicals to C-60. Determination of the rate constants by the spin trap method. Russian Chemical Bulletin 1999;48(12):2344–6.

[8] Gasanov RG, Tumanskii BL. Addition of (Me2CCN)-C-center dot, (Me2CPh)-C-center dot, and (CCl3CH2CHPh)-C-center dot radicals to fullerene C-60. Russian Chemical Bulletin 2002;51(2):240–2.

[9] Walbiner M, Fischer H. Rate constants for the addition of benzyl radical to C-60 in solution. Journal of Physical Chemistry 1993;97(19):4880–1.

[10] Ghosh HN, Pal H, Sapre AV, Mukherjee T, Mittal JP. Formation of radical adducts of C-60 with alkyl and halo-alkyl radicals – transient absorption and emission characteristics of the adducts. Journal of the Chemical Society-Faraday Transactions 1996;92(6):941–4.

[11] Camp AG, Lary A, Ford WT. Free-radical polymerization of methyl-methacrylate and styrene with C(60). Macromolecules 1995;28(23):7959–61.

[12] Stewart D, Imrie CT. Role of C-60 in the free radical polymerisation of styrene. Chemical Communications 1996;11:1383–4.

[13] Arsalani N, Geckeler KE. Radical bulk polymerization of styrene in the presence of fullerene [60]. Fullerene Science and Technology 1996;4(5):897–912.

[14] Cao T, Webber SE. Free radical copolymerization of styrene and C_{60}. Macromolecules 1996;29(11):3826–30.

[15] Chen Y, Lin KC. Radical polymerization of styrene in the presence of C-60. Journal of Polymer Science Part A-Polymer Chemistry 1999;37(15):2969–75.

[16] Kirkwood K, Stewart D, Imrie CT. Role of C_{60} in the free radical polymerization of methyl methacrylate. Journal of Polymer Science Part A-Polymer Chemistry 1997;35(15):3323–5.

[17] Seno M, Fukunaga H, Sato T. Kinetic and ESR studies on radical polymerization of methyl methacrylate in the presence of fullerene. Journal of Polymer Science Part A-Polymer Chemistry 1998;36(16):2905–12.

[18] Seno M, Maeda M, Sato T. Effect of fullerene on radical polymerization of vinyl acetate. Journal of Polymer Science Part A-Polymer Chemistry 2000;38(14):2572–8.

[19] Pabin-Szafko B, Wisniewska E, Szafko J. Carbon nanotubes and fullerene in the solution polymerisation of acrylonitrile. European Polymer Journal 2006;42(7): 1516–20.

[20] Shibaev LA, Egorov VM, Zgonnik VN, Antonova TA, Vinogradova LV, Melenevskaya EY, et al. An enhanced thermal stability of poly(2,6-dimethyl-1,4-phenylene oxide) in the presence of small additives of C_{60} and C_{70}. Polymer Science A 2001;43(2):101–5.

[21] Cataldo F. On the reactivity of C-60 fullerene with diene rubber macroradicals. I. The case of natural and synthetic cis-1,4-polyisoprene under anaerobic and thermo-oxidative degradation conditions. Fullerene Science and Technology 2001;9(4):407–513.

[22] Jipa S, Zaharescu T, Santos C, Gigante B, Setnescu R, Setnescu T, et al. The antioxidant effect of some carbon materials in polypropylene. Materiale Plastice 2002;39(1):67–72.

[23] Troitskii BB, Troitskaya LS, Dmitriev AA, Yakhnov AS. Inhibition of thermo-oxidative degradation of poly(methyl methacrylate) and polystyrene by C-60. European Polymer Journal 2000;36(5):1073–84.

[24] Troitskii BB, Domrachev GA, Semchikov YD, Khokhlova LV, Anikina LL, Denisova VN, et al. Fullerene-C-60, a new effective inhibitor of high-temperature thermooxidative degradation of methyl methacrylate copolymers. Russian Journal of General Chemistry 2002;72(8):1276–81.

[25] Ginzburg BM, Shibaev LA, Ugolkov VL, Bulatov VP. Influence of C-60 fullerene on the oxidative degradation of a free radical poly(methyl methacrylate. Journal of Macromolecular Science – Physics B 2003;42(1):139–66.

[26] Zuev VV, Bertini F, Audisio G. Fullerene C_{60} as stabiliser for acrylic polymers. Polymer Degradation and Stability 2005;90(1):28–33.

[27] Kelar K. Polyamide 6 modified with fullerenes, prepared via anionic polymerization of epsilon-caprolactam. Polimery 2006;51(6):415–24.

[28] Enes RF, Tome AC, Cavaleiro JAS, Amorati R, Fumo MG, Pedulli GF, et al. Synthesis and antioxidant activity of [60]fullerene-BHT conjugates. Chemistry-A European Journal 2006;12(17):4646–53.

[29] Bulgakov RG, Ponomareva Yu G, Maslennikov SI, Nevyadovsky EYu, Antipina SV. Inertness of C_{60} fullerene toward $RO_2^{\bullet}$ peroxy radicals. Russian Chemical Bulletin, International Edition 2005;54(8):1862–5.

[30] Djordjevich A, Bogdanovich G, Dobric S. Fullerenes in biomedicine. Journal of Balkan Union of Oncology 2006;11(4):391–404.

[31] Tsai MC, Chen YH, Chiang LY. Polyhydroxylated C-60, fullerenol, a novel free-radical trapper, prevented hydrogen peroxide – and cumene hydroperoxide-elicited changes in rat hippocampus in-vitro. Journal of Pharmacy and Pharmacology 1997;49(4):438–45.

[32] Shi ZQ, Li YL, Wang S, Fang HJ, Zhu DB. Synthesis and antioxidant properties of polyphenol-fullerenes. Chinese Science Bulletin 2001;46(21):1790–2.

[33] Sun DY, Zhu YS, Liu ZY, Liu GZ, Guo XH, Zhan RY, et al. Active oxygen radical scavenging ability of water-soluble fullerenols. Chinese Science Bulletin 1997;42(9):748–52.

[34] Djordjevic A, Canadanovic-Brunet JM, Vojinovic-Miloradov M, Bogdanovic G. Antioxidant properties and hypothetic radical mechanism of fullerenol C-60(OH)(24). Oxidation Communications 2004;27(4):806–12.

[35] Mirkov SM, Djordjevic AN, Andrich NL, Andrich SA, Kostic TS, Bogdanovic GM, et al. Nitric oxide-scavenging activity of polyhydroxylated fullerenol C-60(OH)(24). Nitric Oxide-Biology and Chemistry 2004;11(2):210–7.

[36] Yu C, Bhonsle JB, Wang LY, Lin JG, Chen BJ, Chiang LY. Synthetic aspects and free-radical scavenging efficiency of polyhydroxylated C-60. Fullerene Science and Technology 1997;5(7):1407–21.

[37] Zhu YS, Sun DY, Liu GZ, Liu ZY, Zhan RY, Liu SY. An ESR study on (OH)-O-center dot-radical scavenging activity of water-soluble fullerenols. Chemical Journal of Chinese Universities-Chinese 1996;17(7):1127–9.

[38] Chiang LY, Lu FJ, Lin JT. Free radical scavenging activity of water-soluble fullerenols. Journal of the Chemical Society-Chemical Communications 1995;12:1283–4.

[39] Yin JL, Lao F, Fu PP, Wamer WG, Zhao YL, Wang PC, et al. The scavenging of reactive oxygen species and the potential for cell protection by functionalized fullerene materials. Biomaterials 2009;30(4):611–21.

[40] Enes RF, Farinha ASF, Tome AC, Cavaleiro JAS, Amorati R, Petrucci S, et al. Synthesis and antioxidant activity of [60]fullerene-flavonoid conjugates. Tetrahedron 2009;65(1):253–62.

[41] Ghanbari B, Khailli AA, Taheri Z, Mohajerani B, Jamarani M, Soleymani. The effect of fullerene C-60 and its amine derivative on the ZDDP antioxidant functionality. Fullerenes, Nanotubes and Carbon Nanostructures 2007;15(6):439–43.

[42] Yang JZ, Alemany LB, Driver J, Hartgerink JD, Barron AR. Fullerene-derivatized amino acids: synthesis, characterization, antioxidant properties, and solid-phase peptide synthesis. Chemistry-A European Journal 2007;13(9):2530–45.

[43] Zeynalov EB, Allen NS. Simultaneous determination of the content and activity of sterically hindered phenolic and amine stabilizers by means of an oxidative model reaction. Polymer Degradation and Stability 2004;85(2):847–53.

[44] Zeynalov EB, Allen NS. An influence of micron and nano-particle titanium dioxides on the efficiency of antioxidant Irganox 1010 in a model oxidative reaction. Polymer Degradation and Stability 2004;86(1):115–20.

[45] Zeynalov EB, Allen NS. Effect of micron and nano-grade titanium dioxides on the efficiency of hindered piperidine stabilizers in a model oxidative reaction. Polymer Degradation and Stability 2006;91(4):931–9.

[46] Zeynalov EB, Allen NS. Modelling light stabilizers as thermal antioxidants. Polymer Degradation and Stability 2006;91(12):3390–6.

[47] Zeynalov EB, Allen NS, Calvet NL, Stratton J. Impact of stabilisers on the thermal catalytic activity of micro- and nano-particulate titanium dioxide in oxidizing condensed mediums. Dyes and Pigments 2007;75(2):315–27.

[48] Allen N.S., Zeynalov E.B., Sanchez K.T., Edge M., Kabetkina Yu.P., Johnson B. Comparative evaluation of the efficiency of a series of commercial antioxidants studied by kinetic modelling in a liquid phase and during the melt processing of different polyethylenes. Journal of Vinyl & Additive Technology, 2009; in press.

[49] Tsepalov VF, Kharitonova AA, Gladyshev GP, Emanuel NM. Determination of the rate constants and inhibition coefficients of phenol antioxidants with the aid of model chain reactions/Determination of rate constants and inhibition coefficients of inhibitors using a model chain reaction. Kinetics and Catalysis 1977;18(5):1034–41. 18(6): 1142-51.

[50] Zeynalov EB, Vasnetsova OA. Kinetic screening of inhibitors of radical reactions. Baku: Elm; 1993.

[51] Van Hook JP, Tobolsky AV. The thermal decomposition of 2,2'-Azo-bisisobutyro nitrile. Journal of the American Chemical Society 1958;80:779–82.

[52] Emanuel NM, Denisov ET, Maizus ZK. Liquid phase oxidation of hydrocarbons. New York: Plenum Press; 1967.

[53] Scott G. Atmospheric oxidation and antioxidants. London: Elsevier; 1993.

[54] Gaponova IS, Fedotova TV, Tsepalov VF, Shuvalov VF, Lebedev YaS. Study of the recombination of cumyl peroxy radicals in liquid and supercooled solutions. Kinetika i Katalys 1971;12:1012–8.

[55] Maillard B, Ingold KU, Scaiano JC. Rate constants for the reactions of free radicals with oxygen in solution. Journal of the American Chemical Society 1983;105(15):5095–9.