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**INFLUENCE OF 2-CHLORO-3-POLYFLUOROALKOXY-[1,4] -
NAPHTHOQUINONES ON THERMAL OXIDATIVE STABILITY OF
POLY(METHYL METHACRYLATE)**

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Abstract: The polymers of methyl methacrylate with 2-chloro-3-polyfluoroalkoxy-[1,4]-naphthoquinones have been synthesized by free radical polymerization method. Their physicochemical properties and thermal characteristics have been studied. It has been shown that using of fluorine-containing [1,4]-naphthoquinones as an antioxidant additive leads to a significant increase in thermal oxidative stability of poly(methyl methacrylate).

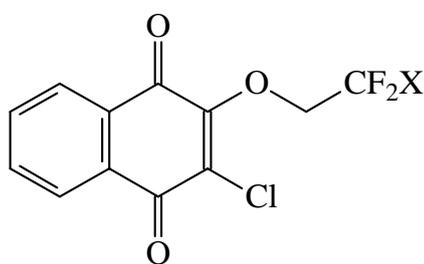
Key words: 2-chloro-3-polyfluoroalkoxy-[1,4]-naphthoquinones, poly(methyl methacrylate), free radical polymerization, heat resistance.

As a result of intensive development of new technologies, the requirements for polymer materials are rising sharply. The most common large-tonnage polymers include the polymers of esters of acrylic and methacrylic acids (for production of organic glasses, contact lenses, etc.) [1, 2]. Among them, a special place is occupied by poly(methyl methacrylate) (PMMA) - a transparent, impact-resistant material with good optical and dielectric properties, strong depletion effect and low water absorption [3, 4]. At the same time, PMMA, like other vinyl polymers, does not possess the required heat- and thermoresistance, which significantly narrows the scope of its practical application at elevated temperatures. To reduce the possibility of destructive processes or slow them down as much as possible, the stabilizers, various modifying additives and antioxidants are introduced into these polymers [3].

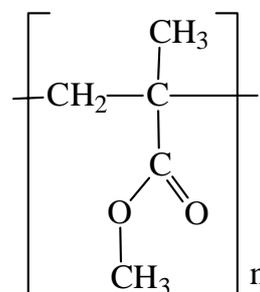
[1,4]-Naphthoquinones are one of the most important classes of organic compounds with antioxidant properties [5]. Among the derivatives of [1,4]-naphthoquinone, fluorine-containing

[1,4]-naphthoquinones are of considerable interest; for this reason it can be used as precursors to obtain antioxidants [6, 7].

In this paper, the authors studied the stabilizing effect on thermal oxidative stability of PMMA 2-chloro-3-polyfluoroalkoxy-[1,4]-naphthoquinones **I-III**, which have different lengths of polyfluoroalkoxy radical (OCH_2CF_3 , $\text{OCH}_2\text{C}_2\text{F}_4\text{H}$, $\text{OCH}_2\text{C}_6\text{F}_{13}$). Compounds **I-III** are low-melting, stable, well-soluble in organic solvents substances, that can be obtained by interaction of commercially available 2,3-dichloro-[1,4]-naphthoquinone and fluorinated alcohols, manufactured commercially [8]. The presence of fluorine-containing substituents in their molecules has a positive effect on solubility in unsaturated monomers, such as alkyl(meth)acrylates, styrene, vinyl acetate, etc.



X = F (I), CF_2H (II), $n\text{-C}_5\text{F}_{11}$ (III)



PMMA

Earlier, it was shown by cyclic voltammetry method that 2-chloro-3-polyfluoroalkoxy-[1,4]-naphthoquinones, studied by authors in aprotic medium, easily undergo stepwise reversible electroreduction (the reduction potential $E^0_1 = -0,35$ V) [9]. This indicates the possibility of using compounds **I - III** for slow down the thermal oxidative degradation of polymers by neutralizing the resulting radicals.

For experimental confirmation of this assumption, PMMA samples with additives of compounds **I, II, III** were synthesized and their thermal characteristics were studied. Free radical polymerization of methyl methacrylate in mass was carried out in evacuated, sealed glass ampoules in the presence of 0.5wt.% of initiating agent - azobisisobutyric acid dinitrile - at 60°C . The polymers are solid transparent glassy yellow samples; its structure was established by IR and mass spectroscopy. The IR spectrum of PMMA with **I** contains the absorption bands specific to units of both methyl methacrylate and compound **I**: $710, 717, 1663, 1676\text{ cm}^{-1}$ (fragments of [1,4]-naphthoquinone); 1142 and 1190 cm^{-1} (CF_3); 1719 cm^{-1} ($\text{C}=\text{O}$ methyl methacrylate). At the same time, there are no absorption bands of stretching vibrations of $\text{C}=\text{C}$ bond at 1645 cm^{-1} $\text{C}=\text{O}$, which were present in IR spectrum of starting methyl methacrylate. IR spectrum of PMMA with **II** also

contains the absorption bands specific to [1,4]-naphthoquinone (709, 716, 1661, 1677 cm^{-1}) and intense bands at 1130 and 1148 cm^{-1} corresponding to CF_2 group. IR spectrum of PMMA with **III** contains intense bands at 1127 and 1145 cm^{-1} (CF_2), and at 1186 and 1198 cm^{-1} (CF_3).

Mass spectral study of methyl methacrylate polymer with 1 mol.% of **I** by direct injection method at ionization energy of 70 eV showed the presence of characteristic traces of ionic destruction of PMMA, m/z , (%): 100 $[\text{M}]^+$ (54), 85 (8), 69 (92), 59 (16), 41 (100), 29 (12), 15 (18) (see Fig. 1). Mass spectrum also contains the molecular ion $290[\text{M}]^+$ 2-chloro-3-(2,2,2-trifluoroethoxy)-[1,4]-naphthoquinone **I** and characteristic traces of its destruction as a result of electron impact: 270, 221, 157, 151, 129, 123, 76, 50 and 18. Due to low concentration of compound **I**, their intensity does not exceed 6%.

It is known that one of the main characteristics of polymers that determine their scope of performance are the glass transition temperature T_g and also the temperature of destruction onset T_d [10, 11]. It should be noted that for comparison, we tested PMMA synthesized without additives and under similar conditions. Evaluation of heat resistance of obtained samples showed that the introduction of **I - III** leads to a decrease in T_g of PMMA, apparently due to polymer loosening by bulky groups. Thus, T_g of PMMA and PMMA with 1 mol.% of compound **I** are 105 and 102°C, respectively. With increase in the content of **I** to 3 mol.%, T_g of polymer is equal 90°C.

The thermoresistance of synthesized polymers was evaluated by temperature of decomposition onset, which was taken to be the temperature at which the weight loss of analyzed sample was 10% of initial one. It was determined by dynamic thermogravimetric analysis (TGA) at a heating rate of 10 °C/min in air. We have shown a significant improvement in thermoresistance of PMMA when compounds **I - III** are used as additives (see Figs. 1, 2). It was found that T_d of polymers with **I - III** increases as increases in the content of fluorine-containing [1,4]-naphthoquinones. For example, T_d of PMMA is 265°C. As can be seen from Fig. 1, T_d of PMMA containing 1 mol.% of compound **I** is equal 305°C, while for the sample with 3 mol.% **I** it is equal 320°C.

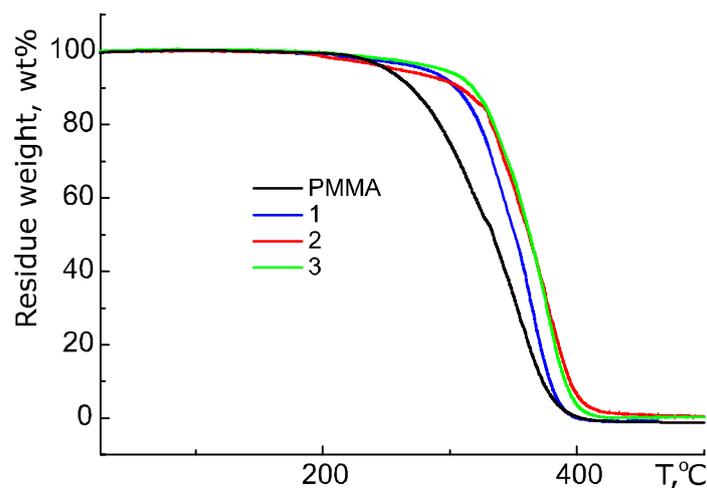


Figure 1. TGA curves of PMMA and PMMA with 1, 2, and 3 mol. % of compound **I**.

T_d of PMMA samples with additions of 1 mol. % of compounds **II** and **III** is 306°C, i.e. its value in this case does not depend on the length of polyfluoroalkyl substituent. For PMMA samples containing 2 mol. % **I–III**, the thermoresistance is higher for polymer with **II** (see Fig. 2).

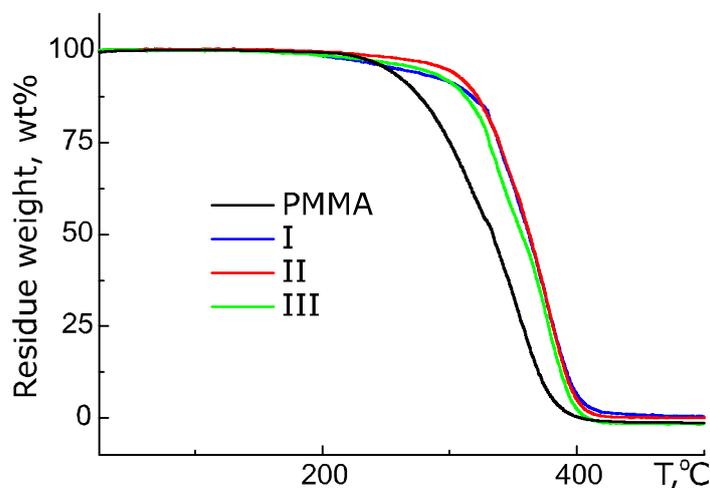


Figure 2. TGA curves of PMMA and PMMA with 2 mol. % of compounds **I**, **II**, **III**.

Thus, a comparison of obtained results with TGA PMMA data indicates a significant improvement in thermal oxidative stability of polymer when fluorine-containing [1,4]-naphthoquinones **I–III** are used as additives. Thermoresistance of PMMA samples with small (1–3 mol. %) content of **I–III** exceeds the thermal resistance of PMMA by 40–55°C.

Experimental part

¹H and ¹⁹F NMR spectra were recorded in CDCl₃ via Bruker Avance 400 spectrometer (at frequency 400 and 376 MHz, respectively). When recording ¹H NMR spectra, Me₄Si was used as an internal standard, ¹⁹F NMR spectra of compounds **I**, **II** - CF₃CO₂H as an external standard, ¹⁹F NMR spectra of compound **III** - CFC₃ (as an external standard). IR spectra were recorded via Bruker Vertex 70 v Fourier spectrometer with resolution of 4 cm⁻¹ in frustrated total internal reflection mode using PIKE Glady ATR attachment with diamond working element. Mass spectra were recorded via Finnigan MAT INCOS 50 quadrupole mass spectrometer (with direct input and ionization energy 70 eV). The glass transition temperature of polymers was determined by thermomechanical analysis via TMA Q400 analyser manufactured by TA Instruments (with probe 2.54 mm in diameter and weighting 100 g) at a sample heating rate of 5°C/min in temperature range 20–250°C. Dynamic thermogravimetric analysis was carried out via Q-1500 derivatograph manufactured by MOM.

2-Chloro-3-polyfluoroalkoxy-[1,4]-naphthoquinones (**I**, **II**, **III**) were synthesized as described in [8].

2-Chloro-3-(2,2,2-trifluoroethoxy)-[1,4]-naphthoquinone (I)

M. p. 105-106 °C. **Founded**, %: C, 50.07; H, 1.98; F, 19.29. C₁₂H₆ClF₃O₃. **Calculated**, %: C, 49.59; H, 2.08; F, 19.61. ¹H NMR (CDCl₃, δ, ppm, J/Hz): 8.18 (m, 1H, Ar), 8.16 (m, 1H, Ar), 7.81 (m, 2H, Ar) - ABCD system; 4.93 (q, 2H, OCH₂, ³J_{H-F}=8). ¹⁹F NMR (CDCl₃, δ, ppm, J/Hz): 2.77 (s, 3F, CF₃).

2-Chloro-3-(2,2,3,3-tetrafluoropropoxy)-[1,4]-naphthoquinone (II)

M. p. 119-120 °C. **Founded**, %: C, 48.58; H, 2.08; F, 23.22. C₁₃H₇ClF₄O₃. **Calculated**, %: C, 48.40; H, 2.19; F, 23.55. ¹H NMR (CDCl₃, δ, ppm, J/Hz): 8.19 (m, 1H, Ar), 8.13 (s, 1H, Ar), 7.81 (m, 2H, Ar) - ABCD system; 6.21 (tt 1H, CF₂H, ²J_{H-F} = 52, ³J_{H-F} = 4); 4.94 (t, 2H, OCH₂, 3J_{H-F} = 11). ¹⁹F NMR (CDCl₃, δ, ppm, J/Hz): -48.21 (s, 2F, CF₂); -61.66 (s, 2F, CF₂).

2-Chloro-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyloxy)-[1,4]-naphthoquinone (III)

M. p. 82-83 °C. **Founded**, %: C, 38.13; H, 1.28; F, 46.04. C₁₇H₆ClF₁₃O₃. **Calculated**, %: C, 37.77; H, 1.12; F, 45.68. ¹H NMR (CDCl₃, δ, ppm, J/Hz): 8.19 (m, 1H, Ar), 8.13 (m, 1H, Ar), 7.82 (m, 2H, Ar) - ABCD system); 5.10 (t, 2H, OCH₂, ³J_{H-F}=11). ¹⁹F NMR (CDCl₃, δ, ppm, J/Hz): -80.71 (t, 3 F, CF₃, ³J_{H-F}=11); -120.56 (td, 2 F, CF₂, ³J_{F-F}=11, ⁴J_{F-F}= 4); -122.08 (m, 2F, CF₂); -122.74 (m, 2F, CF₂); -122.99 (m, 2F, CF₂); -126.09 (t, 2 F, CF₂, ³J_{F-F}=15).

Preparation of PMMA with 2-chloro-3-(2,2,2-trifluoroethoxy)-[1,4]-naphthoquinone (I) in molar ratio of 99: 1

To a solution of 2.50 g of freshly distilled methyl methacrylate (Aldrich, 99%) and 0.072 g of 2-chloro-3-(2,2,2-trifluoroethoxy)-[1,4]-naphthoquinone (**I**) 0.013 g (0.5 wt. %) of azobisisobutyric acid dinitrile was added as a polymerization initiator. Prepared reaction mixture was filtered into a glass ampoule, which was then degassed by freezing three times by immersion in liquid nitrogen followed by thawing in a vacuum, sealed and placed in a thermostat. Polymerization temperature was 60°C. After 4 hours, the ampoule was removed, cooled and opened. The clear yellow solid polymer was dried in a vacuum at 40°C for 24 hours to constant weight.

Preparation of PMMA with 2-chloro-3-(2,2,3,3-tetrafluoropropoxy)-[1,4]-naphthoquinone (II) in molar ratio of 99: 1

Similar to the above described method, from 2.50 g of freshly distilled methyl methacrylate and 0.081 g of 2-chloro-3-(2,2,3,3-tetrafluoropropoxy)-[1,4]-naphthoquinone (**II**) are prepared.

Preparation of PMMA with 2-chloro-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyloxy)-[1,4]-naphthoquinone (III) in molar ratio 99: 1

Similar to the above described method, from 3.30 g of freshly distilled methyl methacrylate and 0.180 g of 2-chloro-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyloxy)-[1,4]-naphthoquinone (**III**) are prepared.

We also synthesized samples of PMMA with compounds **I** - **III** at a molar ratio of 98: 2 and 97: 3.

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