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1,1'-DI[METHACRYLOYLOXY-BIS(TRIFLUOROMETHYL)METHYL] FERROCENE: TWO IN ONE – ANTIOXIDANT AND CROSSLINKER

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Abstract: Copolymers of methyl methacrylate and 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl] ferrocene were synthesized, their structure, solubility and thermal characteristics were studied. It has been established that introduction of 1-3 mol.% of ferrocene-fluorine-containing monomer into poly(methyl methacrylate) chain leads to a significant increase in its thermal and thermo-oxidative stability.

Keywords: 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl] ferrocene, poly(methyl methacrylate), free-radical copolymerization, heat resistance

The service life extension of polymeric materials, as well as expanding the temperature range of their use in various technical apparatus and devices, is of great practical importance. Traditionally, this problem is solved by introducing into polymer the antioxidant additives, which form a mechanical mixture with this polymer. It is known to use the ferrocene and its derivatives as such additive and as one of the most accessible organometallic compounds with a low oxidation potential [1-3]. The ferrocene-containing polymers are used to obtain some organic polyelectrolytes [4], liquid crystals [5] and composite materials [6].

Copolymerization of metal-containing compounds with traditional vinyl monomers makes it possible to modify known polymers in order to increase their functional (including thermal) characteristics [7]. As a rule, the copolymerization reaction proceeds in accordance with a free-radical mechanism, since the corresponding processes are of great practical importance and are easier to study. Thus, it was shown that the introduction of additive (vinyl- or acetylenyl ferrocene) in amount of 10–15% during polymerization (for example, of styrene or isoprene) makes it possible to significantly increase the temperature of thermal destruction of corresponding polymers [8].

Earlier, the authors reported on synthesis of 1-trifluoromethyl-1-ferrocenyl-2,2,2-trifluoroethyl methacrylate (**TFMA**) [9] and "side-chain" homo- and copolymers based on it [10, 11]. The presence of two CF_3 groups and a ferrocenyl substituent in the ester part of its molecule made it possible to obtain α,α -bis(trifluoromethyl)ferrocenyl-containing polymers and copolymers with methyl methacrylate (**MMA**), soluble in organic solvents. It has been shown that introduction of 5 mol. % **TFMA** into polymer chain of poly(methyl methacrylate) (**PMMA**) results in an increase in its thermal and thermo-oxidative stability by 15°C and 55°C , respectively. At the same time, **MMA** polymer with addition of 5 mol. % ferrocene (with its mechanical mixing) is inferior in thermal resistance to copolymers in which ferrocenyl groups (acting as an antioxidant) are attached to polymer chain via a covalent bond (see Fig. 1).

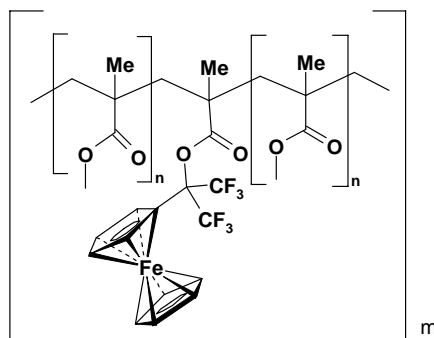
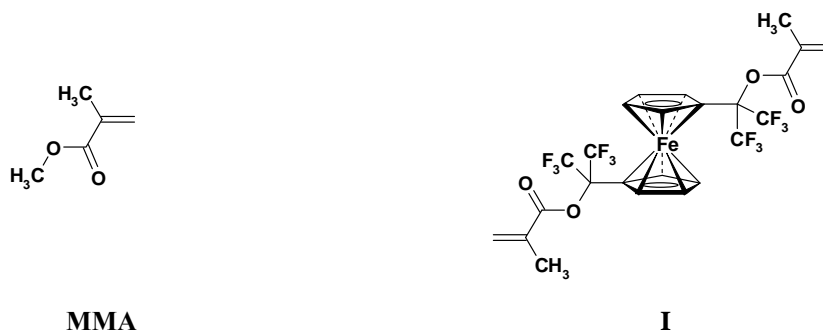


Figure 1.

Such advantages of spatially reticulated polymers as high thermal stability, resistance to solvents and good mechanical properties are widely known [12]. To impart the new practically important properties to known polymers, it seemed appropriate to study the possibility of using bifunctional ferrocene-containing compounds in a synthesis of network polymer systems.

In this paper, the copolymers of **MMA** and 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene (**I**) with various compositions were synthesized by free-radical copolymerization in bulk, and their thermal characteristics were studied.



All copolymers are transparent, solid, glassy yellow specimens, insoluble in organic solvents, alcohols and water. Their structure has been confirmed by elemental analysis and IR spectroscopy. In this case, network copolymers are formed as a result of in situ introduction into polymer chain of resulting **PMMA** 1,1'-bis(1,1,1,3,3,3-hexafluoroisoprop-2-yl) ferrocene-containing component, which acts as a crosslinker (Fig. 2).

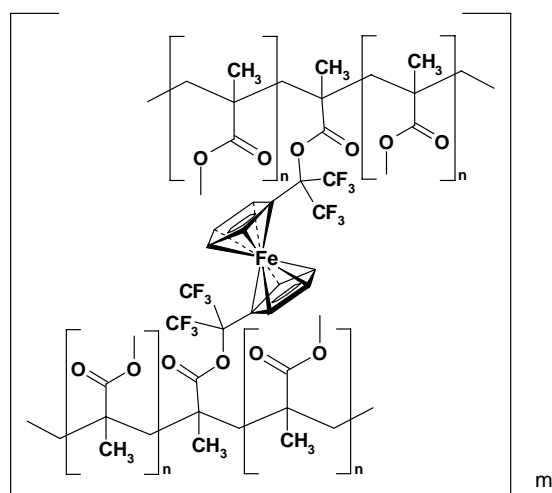


Figure 2.

Due to crosslinking, the inner pore surface decreases. This makes difficult of diffusion and reduces the aerial oxygen content in the copolymer, that capable of causing the destruction of polymer chains under extreme conditions. In turn, the low ionization potential of Fe^{2+} ion in Fe^{3+} in ferrocenyl core, as well as the reversibility of this process without violating the geometry of the molecule [1], also encourage to protection of copolymer from oxidation.

Thermal stability of obtained copolymers was estimated by onset temperature T_d , at which the weight loss of analyzed sample was 10% of initial one. It was determined by dynamic thermogravimetric analysis at heating rate of $10^\circ\text{C}/\text{min}$ in air and in argon atmosphere. The results are shown in Table1.

It was found that T_d of copolymer **MMA** and compound **I**, containing 1 mol. % of **I**-component, is 320°C in air and 360°C in argon. For copolymer, containing 3 mol. % of **I**-component, T_d is 330°C in air and 350°C in argon.

Comparison of obtained results with the data of thermogravimetric analysis of **MMA** homopolymer and copolymers **MMA** with the monomethacrylate derivative of ferrocene **TFMA** indicates a significant improvement in thermal stability, especially under oxidizing conditions (in air), after introduction into **MMA** the dimethacrylate derivative of ferrocene **I** as a comonomer (see Table 1). So, for example, T_d in air for **PMMA** is 265°C , for **MMA** copolymer, containing **TFMA**

with a molar composition 97:3 is 270°C, and for **MMA** copolymer, containing dimethacrylate **I** with a molar composition 97:3 is 330°C. The thermal stability of **MMA** copolymers, containing dimethacrylate **I**, exceeds the thermal stability of **PMMA** by 55-65°C in air, and by 30-40°C in argon. With the same comonomer content in air, the onset temperature of **MMA** copolymers, containing **TFMA** is 45-60°C lower than T_d of **MMA** copolymers, containing dimethacrylate **I**.

Table 1. Thermal characteristics of **PMMA** and **MMA** bulk copolymers, containing **TFMA** and compound **I**

Thermal characteristics of (co)polymer	PMMA	PMMA with additive (5 mol.% of ferrocene)	Copolymer MMA/TFMA , mol.% *			Copolymer MMA/compound I , mol.%	
			99:1	97:3	95:5	99:1	97:3
T_d in air	265	285	275	270	320	320	330
T_d in argon	320	300	330	325	335	360	350

*according to[11]

Thus, the use of ferrocene-fluorine-containing dimethacrylate **I**, which is both an antioxidant and a crosslinker of polymer chains, leads to an increase in thermal resistance and thermo-oxidative stability of **PMMA** by 30-40°C and 55-65°C, respectively. Apparently, compound **I** can be used in a similar way to improve the heat resistance of other vinyl polymers.

Experimental part

^1H and ^{19}F NMR spectra were recorded in CDCl_3 on a Bruker Avance 400 instrument (400,13 and 382 MHz, respectively). Chemical shifts ^1H are given relative to Me_4Si (internal standard), and ^{19}F - relative to $\text{CF}_3\text{CO}_2\text{H}$ (external standard). IR spectra were recorded via Nicolet Magna-750 spectrophotometer. Mass spectra were recorded on a Finnigan MAT INCOS 50 quadrupole mass spectrometer (with direct input, ionization energy 70 e-V). Thermogravimetric analysis was carried out using a MOM Q-1500 derivatograph.

1,1'-Di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene (I) was synthesized as described in [13]. Melting point: 45-46°C (petroleum ether).

Founded, %: C, 44,33; H, 2,71; F, 34,78. $C_{24}H_{18}F_{12}FeO_4$.

Calculated, %: C, 44,06; H, 2,77; F, 34,85.

1H NMR ($CDCl_3$, δ , ppm): 6,19 (br s, 1H, CH_2); 5,73 (br s, 1H, CH_2); 4,49 (br s, 8H, $2C_5H_4$); 1,95 (br s, 6H, $2CH_3$).

^{19}F NMR($CDCl_3$, δ , ppm): -6,28 (s).

Mass spectrum, m/z (I, %): 654 [M] + (100), 586 (34), 570 (10), 226 (27), 195 (19), 69 (7).

Preparation of copolymer MMA and dimethacrylate I at a molar ratio of components 99:1

To a mixture of 2,48 g of freshly distilled **MMA** (Aldrich, 99%) and 0,16 g of 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl] ferrocene (**I**) was added 0,013 g (0,5 wt. %) of dinitrile of azobisisobutyric acid as a copolymerization initiator. The reaction mixture prepared in this way was filtered into a glass ampoule, that was degassed by freezing while immersed in liquid nitrogen, followed by thawing in a vacuum. This procedure was repeated 3 times. After that, this ampoule was sealed off and placed in a thermostat heated to 60°C. After 4 hours, the ampoule was removed, cooled and opened. Transparent yellow solid copolymer was dried under vacuum at 40 °C for 24 hours to constant weight.

Founded, %: C, 59,19; H, 7,68; F, 2,21.

Calculated, %: C, 59,06; H, 7,75; F, 2,16.

The IR spectrum of copolymer contains absorption bands characteristic of both **MMA** component and compound **I**: 3010, 985, 965, 839, 483 cm^{-1} (the ferrocene fragments); 1192 and 1140 cm^{-1} (CF_3); 1724 cm^{-1} ($C=O$ of methyl methacrylate) and 1745 $^{-1}$ ($C=O$ of monomer **I**). There are no absorption bands of stretching vibrations of $C=C$ bonds at 1634 and 1645 cm^{-1} , which were present in the IR spectra of initial monomers.

MMA copolymers with dimethacrylate **I** were synthesized in a similar way at a molar ratio of components 97:3.

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