

Synthesis and properties of the new monomer - 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene

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Abstract: 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene was synthesized by the reaction between 1,1'-di(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)ferrocene and methacryloyl chloride in the presence of sodium hydride in anhydrous dimethylformamide (DMF). Using the physicochemical methods, the structure of 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene and its ability to radical copolymerization with methylacrylate with cross-linked copolymers formation were established.

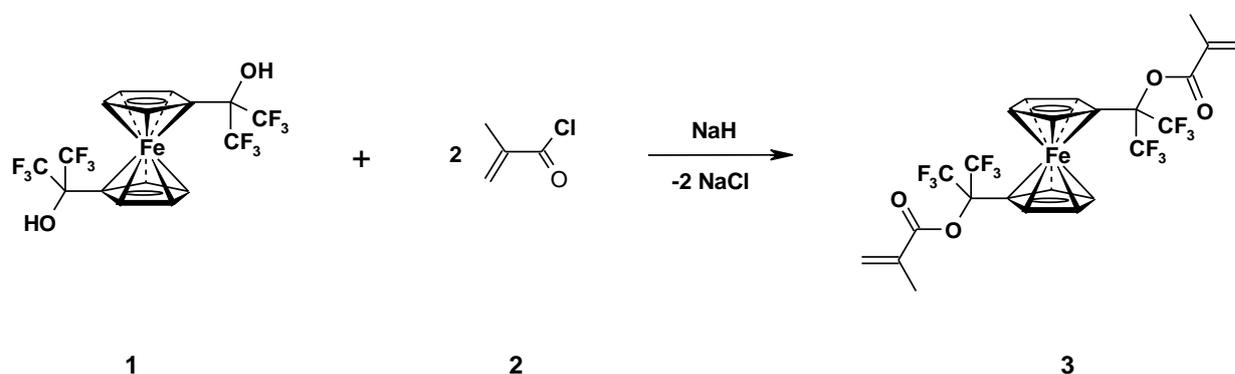
Keywords: 1,1'-di(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)ferrocene, copolymerization, 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene, hydrophobic coatings

The fluorinated polymers, in contrast to its non-fluorinated analogues, are more hydrophobic and oleophobic, highly resistant to oxidation, action of acids and other aggressive media. As a result of these properties, its expansion, as the functional hydrophobic coatings, in the science of materials, aircraft and mechanic engineering, textile industry, everyday usage is increasingly growing up. [1]. Today, the investigations in the sphere of chemistry of coordination polymers are also in intensive progress. Among them, the elementoorganic polymers, which have ferrocenyl substituent in its composition, take a significant place. [2, 3]. Ferrocene-containing polymers are mainstream for glucosic biosensors development [4], for producing of organic polyelectrolytes [5], liquid crystalline polymers [6], compound materials [7]. Earlier we reported the synthesis of 1-trifluoromethyl-1-ferrocenyl-2,2,2-trifluoroethylmethacrylate [8] and preparation of «side-chain» (co)polymers of different composition based on this compound [9]. It was shown that its addition (3-5%) as a comonomer to the reaction mixture while methylmethacrylate polymerization leads to substantial increase in the thermal destruction temperature of the forming polymethylmethacrylate [10].

The aim of this research is a preparation of a new fluorine-containing monomer (Scheme 1) having two methacrylate groups in ferrocene's cyclopentadienyl rings, capable of copolymerization with vinyl monomers to form cross-linked polymers. Furthermore, due to the ferrocene centre in its molecule, screened by two volume tertiary substituents, it is also able to act as an antioxidant, thus extending the temperature range of the application of its copolymers.

Thus, by the reaction of 1,1'-di(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)ferrocene (**1**) with excess of methacryloyl chloride (**2**) corresponding 1,1'- di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene was obtained (**3**).

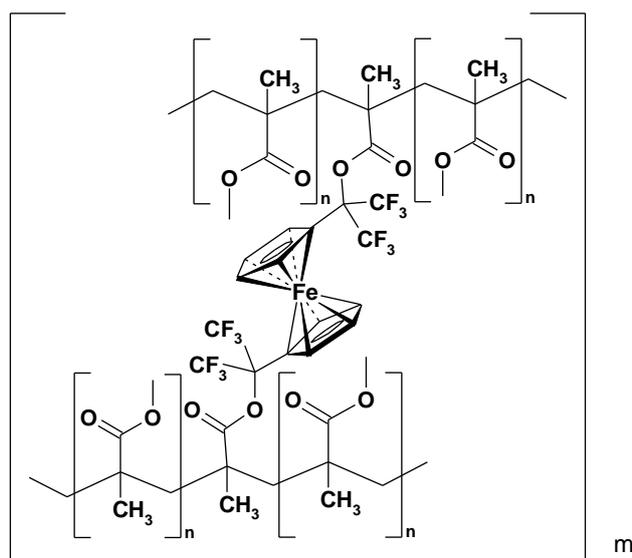
Scheme 1



The reactions between **1** and **2** can be easily carried out in anhydrous DMF in the presence of sodium hydride with the formation of **3** with the yield 77% (Scheme 1). The initial, for this synthesis, dicarbinol **2** was obtained by the reaction of ferrocene with hexafluoroacetone catalyzed by trifluoroacetic acid with the yield 75%, as it was described earlier [11]. It should be noted that carbinol **2** can be obtained without the use of catalyst by prolonged heating of these reagents (180°C, 96 h) [12]. Raw materials for the synthesis of the compound **3** (ferrocene, hexafluoroacetone and methacryloylchloride) are produced in commercial scale, which makes it quite affordable.

Dimethacrylate **3** is a red-orange crystalline compound, non-soluble in water and soluble in almost all organic solvents, stable in storage. Its structure was proved by ^1H NMR and ^{19}F spectra, IR-spectroscopy and elemental analysis data. In the IR-spectra **3** we observe the fringes of absorption, corresponding to ferrocene's centre fragments (zone of valence stretching of CH-vibrations in the field of 3148 cm^{-1} , zone of nonplanar deformation vibration of CH-bonds of substituted Cp-rings in the field of 854 cm^{-1} , zones in the field of $1023\text{--}1079\text{ cm}^{-1}$ which are typical for ferrocene's homoanular derivatives and zone of double degenerated antisymmetric stretching vibration Fe-Cp in the field of 493 cm^{-1}). Besides that, in spectra of compound **3** there are zones of stretching vibrations C=C at 1634 cm^{-1} and deformation vibrations C=C at $969, 984\text{ cm}^{-1}$. We also can observe zones of absorption of C=O and C-O bonds in the field of 1755 и 1135 cm^{-1} correspondingly. Zones at $1224, 1204\text{ cm}^{-1}$, that are typical for CF_3 - groups and zones in the field 2967 cm^{-1} , that are typical for CH_3 - groups also take place.

Due to the presence of two groups with multiple bond in its molecule, dimethacrylate **3** is able to copolymerize with methylacrylate with cross-linked polymers formation in the presence of an initiator of the radical polymerization - azoisobutyronitrile at $60\text{--}70^\circ\text{C}$, similar to 1-trifluoromethyl-1-ferrocenyl-2,2,2-trifluoromethylacrylate [8] (Pic.2).



Pic.2

It was found that an addition of this compound (1%) in the reaction mixture raises the temperature of the thermal destruction (Td) of the resulting polymethacrylate by 50-55°C in the air.

Now it is being studying the possibility of usage of **3** in order to obtain redispersible copolymers [13,14] for raising the contact angle of wetting θ of the hydrophobic coatings formed [15].

Experimental

^1H , ^{19}F NMR spectra were recorded on the instrument «Bruker Avance 400» with the operational frequencies 400,13 MHz, 376,5 MHz correspondingly. Chemical shifts of ^1H were recorded using tetramethylsilane (TMS) as an internal standard, ^{19}F with $\text{CF}_3\text{CO}_2\text{H}$ as an external standard.

IR-spectra were recorded on *Nicolet Magna-750*. Mass-spectra were recorded on *Finnigan MAT INCOS 50* (direct input, ionization energy 70 eV).

1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene (3). To 1,04 g (2 mmol) of carbinol **2** in 5 ml of anhydrous dimethylformamide at the temperature 20°C while mixing 0,08 g (2,5 mmol) of sodium hydride 60% in paraffinic oil was added by portions. When the release of hydrogen is finished, 5 mg of ionol was added to the solution and then 0,29 g (2,5 mmol) of methacryloylchloride was added dropwise at 20°C. The reaction mixture was mixed during 2 h and then poured into 20 ml of cold water. The product of the reaction was extracted by petroleum ether (2x20 ml), extract was dried with anhydrous sodium sulfate, and evaporated in vacuum. The compound **3** was purified by column chromatography, eluent - hexane, 0.9 g of red-orange oil crystallized upon cooling was obtained. Yield 77%. $R_f=0,55$ (CHCl_3), Melting point 45–46°C (petroleum ether).

^1H NMR Spectra δ , ppm: 6,19 (w.s. c, 1H,=CH₂); 5,73 (w.s. c, 1H,=CH₂); 4,49 (br.s., 8H, 2C₅H₄); 1,95 (br.s., 6H, 2CH₃). Spectra NMR ^{19}F , δ , ppm.: -6,28 (s). Mass-spectrum, m/z (I_{rel} , %): 654 [M]⁺ (100), 586 (34), 570 (10), 226 (27), 195 (19), 69 (7). Found, %: C 44,33; H 2,71; F 34,78. C₂₄H₁₈F₁₂FeO₄. Calculated, %: C 44,06; H 2,77; F 34,85. Intensive molecular ion 654 [M]⁺(100) of the compound **3** indicates it's stability, owing to screenage by CF₃-groups, and also abilities to enter the redox processes because of its reversible valence change (Fe²⁺)/(Fe³⁺), without the molecule geometry change.

Conclusions

The new monomer – 1,1'-di[methacryloyloxy-bis(trifluoromethyl)methyl]ferrocene was synthesized and its physicochemical properties were studied. On the methylmethacrylate, taken as an example, there was shown its ability to copolymerization with vinyl monomers, which results in cross-linked copolymers formation. Its addition (1%) to the reaction mixture, raises the thermal destruction temperature of forming polymethacrylate (T_d), on 50-55°C in the air.

Now it is being studying the possibility of use of **3** in order to obtain redispersible copolymers for rising the contact angle of wetting θ of the formed hydrophobic coatings.

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