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New Polymers and Copolymers Based on 1-Trifluoromethyl-1-ferrocenyl-2,2,2-trifluoroethyl Methacrylate[1]

O. A. Mel'nik[a,*], V. I. Dyachenko[a], L. N. Nikitin[a], I. V. Blagodatskikh[a], M. I. Buzin[a], G. Yu. Yurkov[b], Ya. S. Vygodskii[a], S. M. Igumnov[a], and V. M. Buznik[b]

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*
[b] *Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Leninskii pr. 49, Moscow, 119991 Russia*
**e-mail: omel@ineos.ac.ru*

Abstract—Carbon-chain ferrocene-fluoro-containing (co)polymers are synthesized by the free-radical polymerization of 1-trifluoromethyl-1-ferrocenyl-2,2,2-trifluoroethyl methacrylate and its copolymerization with methyl methacrylate in organic solvents and supercritical carbon dioxide. The structures, solubilities, molecular masses, and thermal characteristics of these (co)polymers are studied. It is found that the introduction of 1–5 mol % of the ferrocene-fluoro-containing monomer in the chain of poly(methyl methacrylate) improves its thermal resistance and thermo-oxidative stability.

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Fluoro-containing polymers, in contrast to their nonfluorinated analogs, possess higher lipophilicity and hydrophobicity, high oxidation stability, and resistance to acids and aggressive media. Owing to these valuable properties, they have found wide use in electronics, automobile manufacturing, fiber-optics technology, and other branches of industry [1].

Nowadays, metal-containing polymers represent a large group of high-molecular-mass compounds with diverse properties [2]. An important role in the development of this direction belongs to investigations in the field of coordination polymers, especially those containing iron atoms incorporated into ferrocene moieties [3]. Moreover, such polymers may play the role of precursors of magnetic materials [4–6]. The interest of researchers in these polymers is primarily related to the fact that the ferrocene possesses, apart from its structural features, one of the lowest oxidation potentials [7, 8]. The oxidation of its molecule is nondestructive and is associated only with a change in the valence of its iron atom from Fe^{2+} to Fe^{3+}.

Most carbon-chain polyferrocenes were obtained in the 1970s [9]. Recently, polymers containing ferrocene in side chains have been synthesized via atom-transfer radical polymerization [10–12]. The electrochemical properties of methyl methacrylate copolymers with 2-methacryloyloxyethyl ferrocenyl carboxylate were studied in [13].

Earlier, the ferrocene-fluoro-containing monomer 1-trifluoromethyl-1-ferrocenyl-2,2,2-trifluoroethyl methacrylate (TFMA) was synthesized and its physicochemical properties were investigated [14]. The structure of TFMA is unique because the ester part of its molecule contains, besides two CF_3 groups, a ferrocenyl substituent, which in the polymer may play the role of an antioxidant [9]. The advantages of TFMA are its good solubility in organic solvents and supercritical CO_2 and its low melting point (59°C), close to the decomposition temperatures of such free-radical initiators as AIBN and benzoyl peroxide.

The synthesis of polymers in supercritical CO_2 is an intensively developing direction of "green chemistry." Supercritical CO_2 is the most accessible supercritical medium, is nontoxic and uninflammable, does not sustain combustion, and has low critical parameters [15, 16]. Moreover, CO_2 is, as a rule, an absolutely inert solvent and has no effect on the formation of synthesis products; that is, during polymerization in its medium, the reactions of chain termination and chain transfer to the solvent are absent. There is no need to purify the resulting polymers from the residual solvent, a circumstance that is very important for the production of optical-device elements and special-purpose machinery.

The present study is devoted to the investigation of free-radical homo- and copolymerization of TFMA in organic solvents and supercritical CO_2 and to the investigation of the molecular-mass and thermal characteristics of the resulting (co)polymers.

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[1] The articles in this issue are devoted to the 75th anniversary of the discovery of fluoropolymers.

EXPERIMENTAL

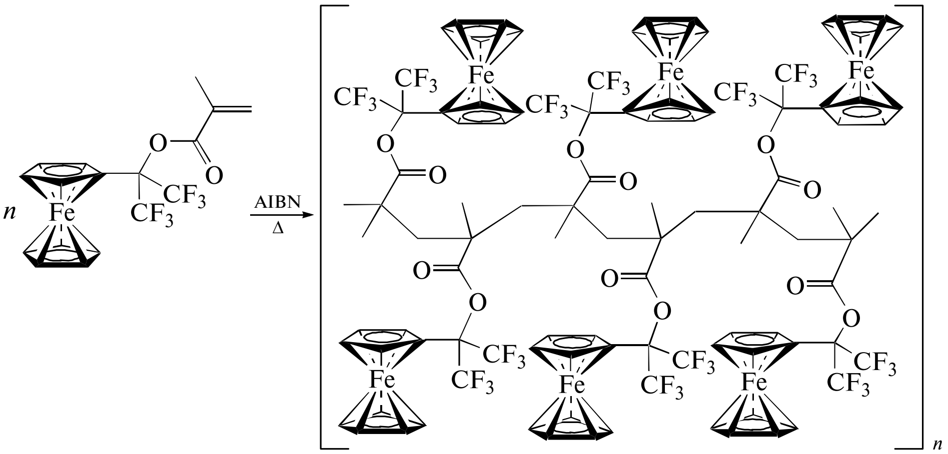
TFMA was prepared as described in [14], and its structure was investigated via elemental analysis, ^{1}H NMR and ^{19}F NMR studies, and IR and UV spectroscopy. Chloroform, benzene, and ethyl acetate were distilled over P_2O_5; DMF was distilled over CaH_2. CO_2 with a degree of purity of 99.995% was used. MMA (Aldrich, 99%) was distilled under reduced pressure. AIBN (Aldrich, 98%) was recrystallized from methanol.

The free-radical polymerization of TFMA in solution and its copolymerization with MMA were performed in the presence of AIBN in evacuated sealed glass ampoules. The synthesis of polymers in the medium of supercritical CO_2 was conducted in a high-pressure reactor as described in [5, 17]. The obtained (co)polymers were reprecipitated from solution in an organic solvent into hexane, washed many times with hexane, and dried in vacuum at 40°C. The conversion of TFMA was determined gravimetrically.

Reduced viscosity values η_{red} were determined at 25°C for 0.5% (co)polymer solutions in benzene. The molecular-mass characteristics of the (co)polymers were analyzed via GPC. Measurements were performed at 30°C in THF at a flow rate of 1 mL/min on an Agilent 1200 device equipped with a refractometric detector and a PL-gel mixC column (Polymer Laboratories). Molecular masses were calculated relative to polystyrene standards. NMR spectra were registered on a Bruker AMX-300 spectrometer in $CDCl_3$ solutions. IR and UV spectra were recorded on a Nicolet Magna-750 and Specord M40 spectrophotometers, respectively. TMA analysis was conducted on a UIR-70M device at a load of 0.2 MPa. A sample was heated at a rate of 5 K/min in the temperature range 20–400°C. Dynamic TGA was performed on a MOM Q-1500 derivatograph at a heating rate of 10 K/min in an argon atmosphere and in air. X-ray powder diffraction was investigated on a Bruker D8 Advance Vario diffractometer equipped with a Ge$K_{\alpha 1}$ monochromator and a LynxEye position-sensitive detector. Electron micrographs of polymers were measured via transmission electron microscopy on a JEOL JEM 1011 device at an accelerating voltage of 80 kV. Samples were deposited both from ethanol dispersions and via pressing of the initial disperse powder into a copper grid covered with polyvinylformal.

RESULTS AND DISCUSSION

The free-radical polymerization of TFMA was conducted in the presence of AIBN in various solvents. In benzene, ethyl acetate, and chloroform, polymerization proceeds under homogeneous conditions, while in DMF, the polymer precipitates as a yellow powder.



In the ^{1}H NMR spectrum of the polymer, signals due to protons of CH_2 groups (5.71 and 6.19 ppm) are absent, while signals due to protons of $-CH_2-$ groups appear at 1.31 and 1.72 ppm. The ^{19}F NMR spectrum shows a single signal in the region of $\delta = 10.25$ ppm (CF_3).

The IR spectrum of the polymer exhibits absorption bands corresponding to ferrocene fragments: a band at 3099 cm^{-1} due to stretching vibrations of CH groups, a band at 822 cm^{-1} due to out-of-plane bending vibrations of CH bonds of the substituted Cp ring, bands at 1000–1100 cm^{-1} that are characteristic of homoannular ferrocene derivatives, and bands at 485 cm^{-1} due to doubly degenerate antisymmetric stretching vibrations of Fe–Cp bonds. In this spectrum, there are no absorption bands at 1637 cm^{-1} that correspond to stretching C=C vibrations and no bands at 952 cm^{-1} that correspond to bending C=C vibrations and that were present in the IR spectrum of the initial monomer. In addition, the IR spectrum of the polymer shows absorption bands at 1773 and

1146 cm^{-1} (C=O and C–O ester bonds), intense bands at 1208 and 1215 cm^{-1} (CF_3), and bands in the range 2854–2995 cm^{-1} ($–CH_2–$ and CH_3 groups). The electronic absorption spectra of the polymer (a solution in $CHCl_3$) in the UV and visible ranges exhibit three absorption maxima typical for ferrocene: at 251, 330, and 443 nm.

The dependence of monomer conversion on polymerization time was investigated in benzene at 60 and 70°C (Fig. 1). It is seen that close-to-ultimate conversions are attained already after polymerization for ~16 h. After 36 h at 60 and 70°C, the polymer yields are 86 and 92%, respectively. As temperature is increased by 10°C, polymerization slightly accelerates owing to an increase in the rate of initiation.

Table 1 lists the data on the synthesis of PTFMA in various solvents. The rate of polymerization in benzene is higher than those in the other used solvents: the polymer yield attained over 8 h is 52% (experiment 1). Polymerization performed in supercritical CO_2 under the same conditions produces polymers insoluble in organic solvents with yields of 8 and 10% at 60 and 70°C, respectively (experiments 5, 6).

Molecular-mass characteristics of the homopolymers were estimated via GPC (Table 1). The polymer with the highest M_w value was obtained in ethyl acetate (experiment 2), while the polymer with the lowest M_w value was synthesized in chloroform (experiment 4). Polydispersity coefficients M_w/M_n of the polymers were in the range 1.58–2.03, as is typical for free-radical polymerization. In the case of homogeneous polymerization (experiments 1, 2, 4), the polydispersity coefficients were lower than that of PTFMA precipitated from the reaction medium during the synthesis (experiment 3).

The obtained polymers are soluble in benzene, toluene, chloroform, ethyl acetate, and THF; partially soluble in acetone; and insoluble in DMF, DMSO, hexane, diethyl ether, lower alcohols, and water. According to X-ray powder diffraction, all the polymers are amorphous. Figure 2 presents the electron micrograph of PTFMA synthesized in DMF (Table 1, experiment 3). Note that the synthesis gives rise to associates of ferrocene-containing fragments within the uniform PTFMA polymer with sizes not above 5 nm along with associates with sizes of 1–2 nm. It may be concluded that a bimodal particle-size distribution with maxima at 2 and 5 nm is observed for this sample.

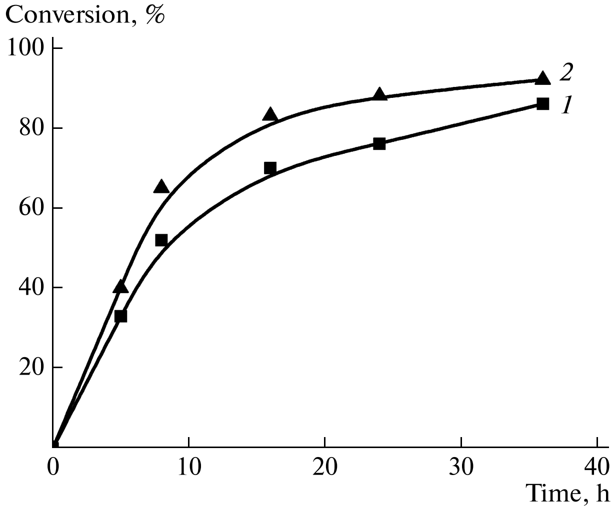


Fig. 1. Conversion of TFMA vs. time of polymerization at (*1*) 60 and (*2*) 70°C. [AIBN] = 2 wt % and a 20% monomer solution in benzene.

Heat resistances and thermal stabilities of PTFMA samples were evaluated. According to the TMA data, the glass-transition temperature of the polymer prepared in benzene is 150°C. Dynamic TGA curves obtained for this polymer are presented in Fig. 3. The decomposition of PTFMA proceeds via several stages. The thermal and thermal-oxidative stabilities of the polymer are the same. The onset temperature of destruction processes, which was accepted to be the temperature corresponding to 10% weight loss ($T_{10\%}$), is 185°C. However, in the first stage of PTFMA decomposition in air (curve *1*), the weight loss for the

Table 1. The yield and molecular-mass characteristics of PTFMA obtained in various solvents ([AIBN] = 2 wt %, [TFMA] = 20 vol %, a reaction time of 8 h, and $T = 60°C$)

Experiment	Solvent	Polymer yield, %	$M_w \times 10^{-3}$	M_w/M_n
			GPC	
1	Benzene	52	28.5	1.77
2	Ethyl acetate	24	52.8	1.77
3	DMF	35	38.9	2.03
4	Chloroform	6	17.2	1.58
5	Supercritical CO_2	8	Insoluble polymer	
6*	The same	10	The same	

Note: *$T = 70°C$.

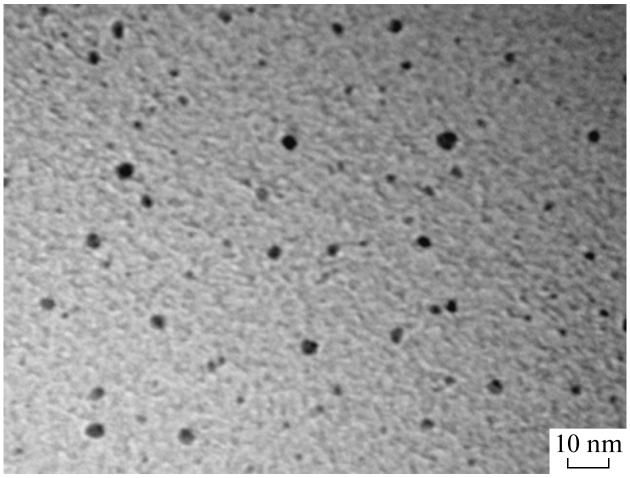
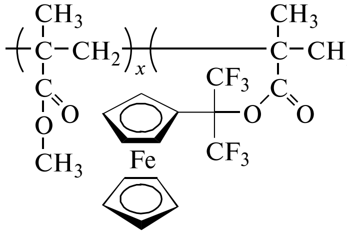


Fig. 2. Electron micrograph of the PTFMA sample synthesized in DMF.

sample is much lower than that in the first stage of PTFMA decomposition in the inert atmosphere (curve *2*). Obviously, thermo-oxidative processes proceeding during the effect of atmospheric oxygen promote the formation of a thermally stable structure in the sample with the onset temperature of decomposition in the range 280–300°C.

The copolymerization of metal-containing compounds with common vinyl monomers makes it possible to modify known polymers and impart functional properties to them [18]. In the present study, along with the homopolymerization of TFMA, its free-radical copolymerization with MMA in a benzene solution and in bulk was performed in the presence of AIBN at 60°C.



The copolymers are yellow powders or transparent glassy samples. The structures of the copolymers were studied via elemental analysis, ^{19}F NMR and IR spectroscopy, and GPC. In the ^{19}F NMR spectrum, there is one signal at $\delta = 10.15$ ppm (CF_3). The IR spectra of the copolymers contain absorption bands characteristic of both MMA and TFMA. The intense absorption band at 1732 cm^{-1} is due to vibrations of ester C=O groups of MMA, while the band at 1767 cm^{-1} is characteristic of the same group of TFMA. CF_3 groups in TFMA absorb at 1205 and 1215 cm^{-1}. In addition, the spectra show absorption bands corresponding to ferrocene fragments: a band at 3025 cm^{-1} due to the stretching vibrations of CH groups, bands at 1063 and 1075 cm^{-1} due to homoannular ferrocene derivatives, and bands at 484 cm^{-1} due to doubly degenerate antisymmetric stretching vibrations of Fe–Cp bonds. There are no absorption bands at 1640 cm^{-1} that correspond to the stretching vibrations of C=C bonds and no bands at 952 cm^{-1} that correspond to the bending vibrations of C=C bonds and that were present in the IR spectrum of the initial monomer.

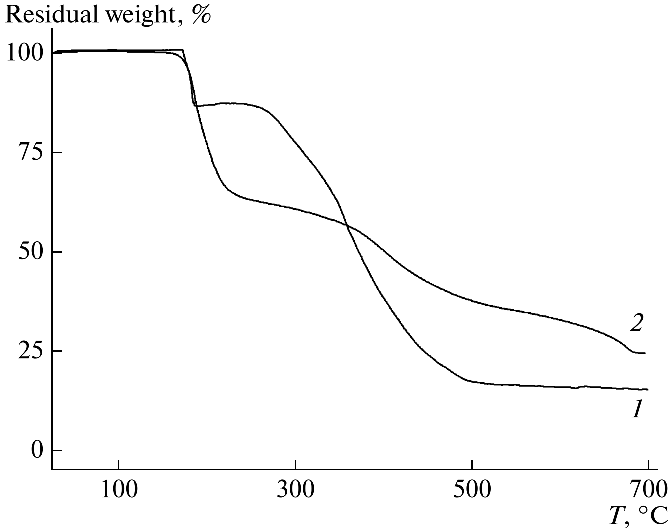


Fig. 3. TGA curves of the PTFMA sample obtained in ethyl acetate in (*1*) air and (*2*) the argon atmosphere.

Table 2 summarizes the data on the copolymerization of MMA and TFMA monomers in benzene solutions. The yields of the copolymers were from 65 to 76%. At a low content of TFMA (5 or 10 mol %) in the monomer feed, the copolymer composition practically coincides with the composition of the monomer feed. As the molar fraction of TFMA in the initial reaction mixture is increased, the amount of MMA units in the copolymer tends to increase. According to the GPC studies, the copolymers feature monomodal molecular-mass distributions. The values of M_w are within (86–250) × 10^3, and the polydispersity coefficients for the copolymers are in the range 1.75–3.50. The reduced viscosity and molecular-mass values decrease with an increase in the content of TFMA units in a chain.

The copolymers are soluble in benzene, toluene, chloroform, methylene chloride, ethyl acetate, and THF; partially soluble in acetone; and insoluble in DMF, DMSO, hexane, diethyl ether, lower alcohols, and water.

The thermal characteristics of bulk copolymers of MMA and TFMA (1–10 mol %) were investigated. For comparison, PMMA samples obtained via the polymerization of MMA in the presence of ferrocene and without it under similar conditions were tested. The copolymer containing 1 mol % TFMA has a higher glass-transition temperature than PMMA

Table 2. Copolymerization of MMA (M_1) and TFMA (M_2) in benzene ([AIBN] = 1 wt %, [M] = 20 vol %, a reaction time of 8 h, and $T = 60°C$)

M_2, mol %	Yield, %	Content F, wt % (found/calcd)	Content Fe, wt % (found/calcd)	m_2, mol %	η_{red}, dL/g	$M_w \times 10^{-3}$	M_w/M_n
5	65	4.78/4.91	2.52/2.41	5	0.54	250	3.50
10	68	8.59/8.64	4.38/4.23	10	0.50	–	–
30	68	14.60/17.45	6.85/8.55	22	0.27	95.3	1.75
50	76	19.17/21.92	9.60/10.74	38	0.10	86.0	1.91

(110 and 100°C, respectively). With further increases in the content of TFMA units, the glass-transition temperatures of the copolymers decrease to 95°C obviously owing to loosening of polymer chains by bulky substituents. It was found that the copolymers containing 5 mol % TFMA show the highest thermal stabilities: Their $T_{10\%}$ values in air increase by 55°C relative to that of PMMA (Fig. 4a, curves *1*, *3*). If TGA is conducted in the inert atmosphere, the $T_{10\%}$ values increase by 15°C (Fig. 4b, curves *1*, *3*). A positive contribution of ferrocene moieties chemically bound to the polymer matrix likewise makes itself evident in the high-temperature range; as a consequence, thermal and thermo-oxidative stabilities of the copolymers are higher than those of PMMA samples containing the same amounts of ferrocene additives (Fig. 4, curve *2*).

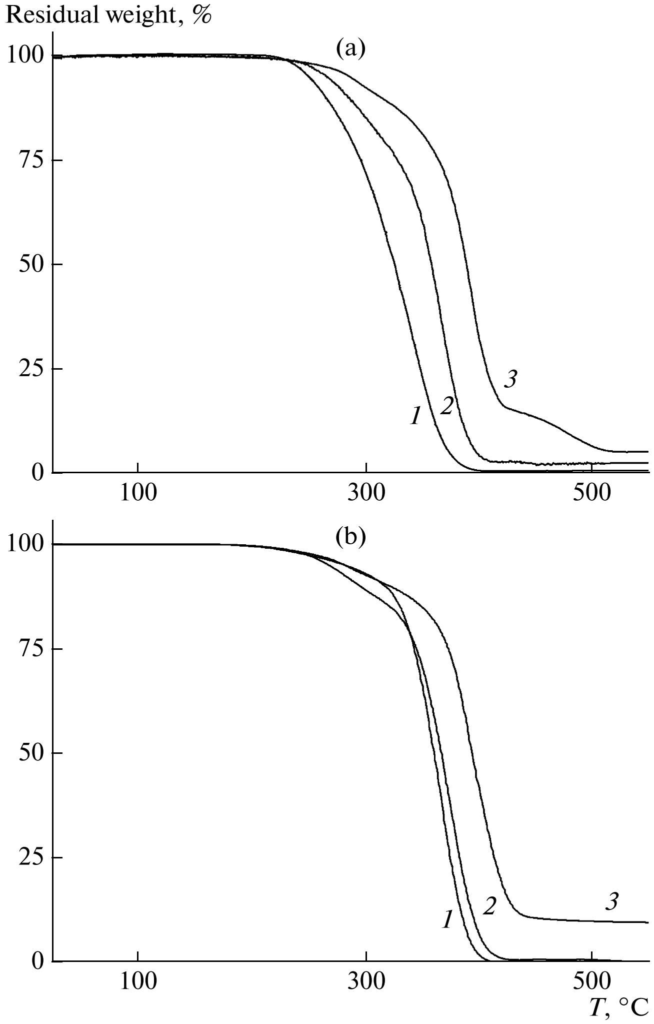


Fig. 4. TGA curves of (*1*, *2*) PMMA samples obtained (*1*) in the absence of ferrocene and (*2*) in the presence of 5 mol % ferrocene and (*3*) the copolymer of MMA with 5 mol % TFMA in (a) air and (b) the argon atmosphere.

Thus, new carbon-chain ferrocene-fluoro-containing polymers and copolymers with MMA have been synthesized through the free-radical (co)polymerization of 1-trifluoromethyl-1-ferrocenyl-2,2,2-trifluoroethyl methacrylate in organic solvents and supercritical carbon dioxide.

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