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Ring-opening polymerization of octamethylcyclotetrasiloxane using 3d metal trifluoroacetate complexes

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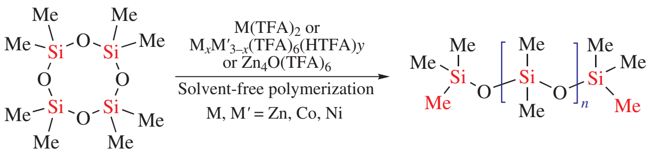
3d-Metal trifluoroacetate complex-catalyzed ring opening polymerization of octamethylcyclotetrasiloxane affords polydimethylsiloxanes whose molecular weight can be controlled by the nature of 3d metal complexes, in particular, by their structural type, and by the polymerization conditions. The best results were achieved using tetranuclear zinc oxotrifluoroacetate as the catalyst at a temperature of 75 °C and a reaction time of 35 h.



Keywords: polysiloxanes, trifluoroacetate complexes, ring-opening polymerization, octamethylcyclotetrasiloxane, Lewis acids.

Polyorganosiloxanes, in particular polydimethylsiloxanes (PDMS), are among the most important large-tonnage polymers[1] that are widely used in construction, engineering, the textile and paper industries, energetics, medicine and perfumery.[2–4] Over the past decades, polyorganosiloxanes have become popular in organic electronics and photonics,[5,6] 3D printing,[7–9] gas separation,[10,11] and drug delivery.[12,13] Up to now, a large number of methods for synthesizing polyorganosiloxanes have been developed, which can be classified into hydrolytic condensation of alkylchlorosilanes and alkylalkoxysilanes, polycondensation of oligomeric oligo(organosiloxane) diols, as well as anionic and cationic polymerization of cycloorganosiloxanes.[14–20] However, application of the majority of catalysts requires additional purification of the resulting polymer products, which limits their use, in particular, in perfumery products and in medicine.[21] The studies on potential of p-element triflate complexes of in the polymerization of octamethylcyclotetrasiloxane (D4) revealed[22] that the use of such complexes makes it possible to obtain high molecular weight polymers; in addition, they are not dangerous and can be easily removed from the resulting polymers.

Table 1 Composition of trifluoroacetate complexes used in polymerization of octamethylcyclotetrasiloxane D4 and GPC data of the polymers obtained.

Catalyst[a]	Structural type[b]	D4 : cat.	M_n[c]/ 10^{-2}	M_p[d]/ 10^{-2}	PDI[e]	L/D[f]
HTFA		1 : 0.2	205	233.5	1.77	83 : 17
$Co(TFA)_2·4H_2O$	I	1 : 0.1	94	144	1.62	30 : 70
$Ni(TFA)_2·4H_2O$	I	1 : 0.1	498	547	1.63	14 : 86
$Zn(TFA)_2·4H_2O$	I	1 : 0.1	804	1130	1.66	46 : 54
$[Co_3(TFA)_6(HTFA)_6](HTFA)$	II	1 : 0.033	121	144	1.65	86 : 14
$Ni_3(TFA)_6(HTFA)_6$	II	1 : 0.033	257	343	1.60	55 : 45
$Na[Co_3F(TFA)_6(HTFA)_3]$	III	1 : 0.07	170	290	1.50	34 : 66
$Na[Ni_3F(TFA)_6(HTFA)_3]$	III	1 : 0.07	425	592	1.72	50 : 50
$[ZnCo(TFA)_4(HTFA)_2]_n$ **1**	IV	1 : 0.1	121	207	1.75	91 : 9
$[Zn_{1.4}Ni_{0.6}(TFA)_4(HTFA)_2]_n$ **2**	IV	1 : 0.1	101.3	173	1.76	90 : 10
$Zn_4(\mu_4–O)(TFA)_6$	V	1 : 0.033	1036	996	1.59	86 : 14

[a] Synthesis of catalysts is given in ref. 23, except for new compounds **1** and **2**. The catalyst amount was calculated relative to one equivalent of trifluoroacetic acid in the complex. [b] I, mononuclear, molecular, resistant to air moisture and ligand exchange; II, trinuclear, molecular, react with release of HTFA; III, trinuclear, ionic, react with release of HTFA; IV, polynuclear, react with release of HTFA; V, tetranuclear, molecular, does not release HTFA. [c] M_n is the number average mass. [d] M_p is the peak mass. [e] PDI is the polydispersity index. [f] L/D is the ratio of linear and cyclic products according to the integral intensities of GPC peaks.

In this work, ring opening polymerization (ROP) of D4 was studied using some known[23] trifluoroacetate complexes of cobalt, nickel and zinc as well as two herein prepared mixed complexes **1** and **2** as the catalysts (Table 1, for the synthesis of the catalysts see Online Supplementary Materials). New complexes $[ZnCo(TFA)_4(HTFA)_2]_n$ **1** and $[Zn_{1.4}Ni_{0.6}(TFA)_4(HTFA)_2]_n$ **2** were studied by X-ray crystallography.[†] The metal ratio in them was

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[†] *Crystallographic data for* **1**. Crystals of $C_{12}H_2F_{18}O_{12}ZnCo$ (M = 1604.84) are monoclinic, space group $P2_1/c$, at 150 K: $a = 8.8458(8)$, $b = 15.1341(13)$ and $c = 18.2036(16)$ Å, $\beta = 100.7850(10)°$, $V = 2393.9(4)$ Å^3, $Z = 4$, $d_{calc} = 2.226$ g cm^{-3}, μ(MoKα) = 1.892 cm^{-1}, $F(000) = 1548$. 19756 reflections were measured and 4693 independent reflections ($R_{int} = 0.0290$) were used in the further refinement. The refinement converged to $wR_2 = 0.1591$ and GOF = 1.032 for all independent reflections [$R_1 = 0.0637$ was calculated against F for 4693 observed reflections with $I > 2\sigma(I)$].

Crystallographic data for **2**. Crystals of $C_{12}H_2F_{18}O_{12}Zn_{1.4}Ni_{0.6}$ ($M = 1604.40$) are monoclinic, space group $P2_1/c$, at 120 K: $a = 8.8234(4)$, $b = 15.0715(6)$ and $c = 18.1278(8)$ Å, $\beta = 101.0720(10)°$, $V = 2365.80(18)$ Å^3, $Z = 4$, $d_{calc} = 2.252$ g cm^{-3}, μ(MoKα) = 2.009 cm^{-1}, $F(000) = 1560$. 28040 reflections were measured and 6914 independent reflections ($R_{int} = 0.0267$) were used in a further refinement. The refinement converged to $wR_2 = 0.1511$ and GOF = 1.042 for all independent reflections [$R_1 = 0.0603$ was calculated against F for 5816 observed reflections with $I > 2\sigma(I)$].

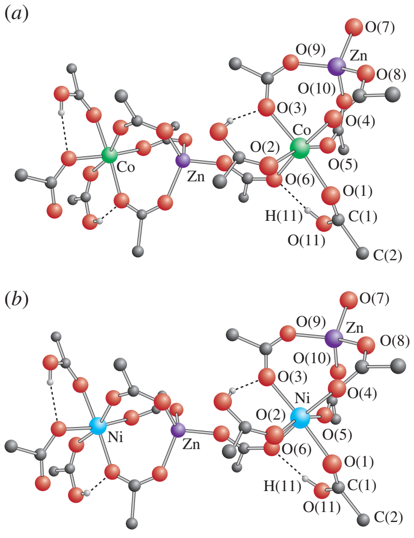


Figure 1 Crystal structure of (*a*) $[\mathrm{ZnCo(TFA)_4(HTFA)_2}]_n$ **1** and (*b*) fragment of crystal of complex **2** with $[\mathrm{ZnNi(TFA)_4(HTFA)_2}]_n$ composition (fluorine atoms of the $\mathrm{CF_3}$ groups are not shown).

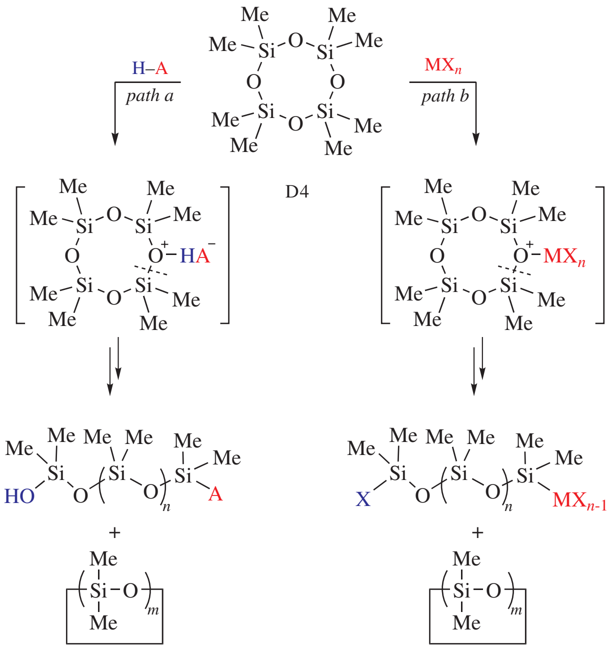
additionally confirmed by X-ray fluorescence analysis of the monocrystals. Compounds **1** and **2** have the same structural types as the structure of zinc hydrogen trifluoroacetate $[\mathrm{Zn_2(TFA)_4(HTFA)_2}]_n$[23] and consist of infinite $[\mathrm{M(HTFA)_2(HTFA)_3M(HTFA)}]_n$ chains bound by the van der Waals interactions [Figure 1(*a*),(*b*)].

Each chain is formed by two crystallographically independent metal atoms located in different coordination environments [octahedral in M(1) and tetrahedral in M(2)] and interconnected by three [M(1)–O(3)–O(9)–M(2), M(1)–O(5)–O(10)–M(2), M(1)–O(4)–O(8)–M(2)] or one [M(2)–O(7)–O(6)–M(1)] bridging trifluoroacetate groups. In both structures of $[\mathrm{ZnCo(TFA)_4(HTFA)_2}]_n$ **1** and $[\mathrm{ZnZn_{0.4}Ni_{0.6}(TFA)_4(HTFA)_2}]_n$ **2**, the alloying metal atoms (Co and Zn) selectively occupy octahedral positions, while the zinc atoms occupy tetrahedral ones, and a fraction of octahedral ones in the case of **2**. The population of octahedral positions by zinc atoms in **2** is statistical.

The coordination environment of metal atoms is a highly distorted octahedron (**2**) or tetrahedron (**1**) constructed from oxygen atoms of trifluoroacetate groups or trifluoroacetic acid molecules.

Analysis of the crystalline structures of **1** and **2** containing different metal atoms in the M(1) position clearly shows that the distortion of the polyhedron is preserved, the ranges of angles are similar, and the difference in the bond lengths is due solely to the difference in the atomic radii.

Cyclosiloxanes can be cleaved by the cationic mechanism either with Brønsted acids or with Lewis acids,[24] which determines the stage of cleavage of the cyclosiloxane ring (Scheme 1,[4] pathways *a* or *b*, respectively).



Scheme 1

The effect of the trifluoroacetate complexes of 3d metals can be described by two different schemes or by their combination. On the one hand, trifluoroacetic acid can be formed *in situ* if complexes that are prone to ligand-exchange reactions, which determines the Brønsted acidity of the trifluoroacetate complexes. On the other hand, the Lewis acidity of a 3d metal atom can be a decisive factor in the polymerization process. We cannot exclude a complex mechanism of action of trifluoroacetate complexes. For example, at the first stage, the Lewis acidity of the metal complexing agent may be in effect, and, as a result, trifluoroacetic acid may be displaced from the coordination sphere. After that, the released acid molecule can initiate the polymerization.[‡]

After purification, the molecular weight characteristics of the polymers thus obtained (see Table 1) were studied by gel-permeation chromatography (GPC). The L/D ratio shows the presence of linear (L) and cyclic (D) products in the reaction mixture, which is typical of PDMS polymerization. The presence of cyclic products can indicate either unreacted source D4 in the reaction mixture or generation of cyclic products during polymerization.

A consistent increase in the number-average and weight-average masses of polymerization products in the presence of trifluoroacetate complexes of structural type I indicates that the activity of cationic polymerization catalysts increases with an increase in the Lewis activity of complexing atoms in the Co – Ni – Zn series. If trifluoroacetate complexes of structural types II–IV are used, the influence of the Lewis activity of the complexing atom is also observed, however an additional effect arises due to structural features. Thus, in the case of trifluoroacetate complexes of structural type II, the molecular weights of the polymers obtained are determined by a combination of factors, namely, the presence of trifluoroacetic acid in the outer sphere of the complex and a greater steric hindrance of the metal atom. The ionic structure of structural type III complexes promotes the formation of oxonium intermediates, which act as active centers of growth in the cationic polymerization in the presence of Lewis acids. Therefore, sodium fluorotrifluoroacetate metal complexes show the highest conversion compared to mono- and polynuclear molecular complexes. The steric accessibility of the central metal atom in a complex increases as the coordination number decreases to 4. As an example, zinc trifluoroacetate complex $[\mathrm{Zn_2(TFA)_4(HTFA)_2}]_n$, which contains

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The measurements were performed on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2.[16] The hydrogen atom positions were fixed geometrically at calculated distances and allowed them to ride on the parent atoms.

CCDC 1872502 and 1872503 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[‡] The polymerization procedure is presented in Online Supplementary Materials.

polymer chains of two crystallographically independent zinc atoms in different coordination environments, *viz.*, octahedral Zn(1) and tetrahedral Zn(2), was chosen.

To study the catalytic properties of zinc atoms located only in the tetrahedral environment, it is necessary to reduce the catalytic activity of zinc atoms in the octahedral positions. This can be achieved by selective replacement of Zn(1) atoms by atoms of other 3d metals (cobalt and nickel were used in this study). Selective replacement is possible due to a gain in the crystal field stabilization energy of the ligands in the octahedral environment of metals, which differs from that in the d^{10} (Zn) electronic configuration. The polynuclear heteroatomic trifluoroacetate complexes **1** and **2** are inorganic polymer structures with rigid chains. In the initiation step of the polymerization, a coordinated attack of catalytically active centers (Zn atoms) of D4 molecules occurs. The relatively low molecular weights of the polymers in this case can be explained by the rigidity of the complex structure, which suppresses the growth of polymer chains due to steric hindrance. The similar molecular weight characteristics of polymer products in the case of complexes **1** and **2** indicate that the polymerization is mainly activated by zinc atoms located in positions M(2).

Structural type V is represented by the zinc compound as the strongest Lewis acid, while all the atoms of the complexing metal are only in a tetrahedral environment. In this case, both the highest molecular weight and a high degree of conversion of the starting cyclosiloxane are achieved. X-ray fluorescence analysis showed the absence of any traces of the zinc catalyst within the detection limit of the X-ray spectrometer.

To conclude, the first acidic heteronuclear complexes $[ZnCo(HTFA)_4(HTFA)_2]_n$ and $[ZnZn_{0.4}Ni_{0.6}(TFA)_4(HTFA)_2]_n$ have been obtained and structurally characterized. The ring opening polymerization with trifluoroacetate complexes of 3d metals occurs predominantly involving the Lewis acid mechanism. An increase in the ionicity of the complexes increases the conversion and the time to reach equilibrium. Tetranuclear zinc oxotrifluoroacetate (structural type V) demonstrates the best catalytic activity.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.014.

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