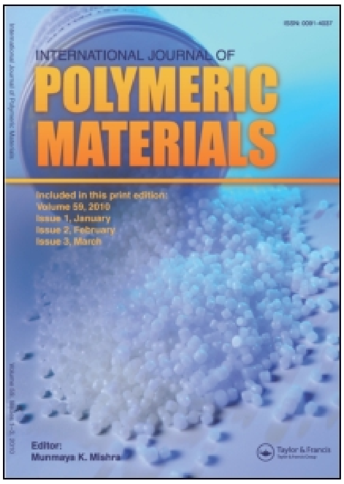

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Synthesis and Properties of Poly(chelato)dititaniumoxy-dimethylsiloxanes

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Synthesis of polytetrakis(chelato)dititaniumoxydimethylsiloxanes by virtue of heterofunctional polycondensation reaction between α,ω-dihydroxyoligodimethylsiloxane and tetrakis(chelato)dibutoxydititaniumoxane and its properties are reviewed.

Keywords: Heterofunctional polycondensation; polytetrakis(chelato)dititaniumoxydimethylsiloxane; poly(chelato)dititaniumoxydimethylsiloxane

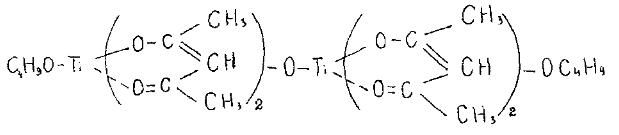
INTRODUCTION

To synthesize polytetrakis(chelato)dititaniumoxydimethylsiloxanes of linear structure we utilized heterofunctional polycondensation (HFC) of α, ω-dihydroxyoligodimethylsiloxanes with tetrakis(chelato)dibutoxydititaniumoxanes.

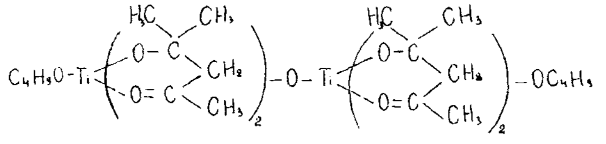
HFC of α, ω-dihydroxyoligodimethylsiloxanes and metal alcoxy- derivatives were initially elaborated by K. Andrianov, A. Zhdanov [1], and subsequently by M. Wick [2]. Polymers obtained by virtue of this method are elastic substances soluble in organic solvents and characterized by significant reactivity.

Above mentioned method is of great interest since silicoorganic dioles ($n > 6$) do not form cycles during polycondensation [1,2], and thus products of the reaction are only linear polymers.

In HFC reaction we utilized tetrakis(chelato)dibutoxydititaniumoxanes, especially tetrakis(acetylacetonate)dibutoxydititaniumoxane



and tetrakis(dimethylacetonylcarbinolate)dibutoxydititaniumoxane



as partners of α,ω-dihydroxyoligodimethylsiloxanes.

EXPERIMENTAL PART

Initial α,ω-dihydroxyoligodimethylsiloxanes were synthesized by telomerization reaction of octamethylcyclotetrasiloxane and dimethyldichlorsilane [3] followed by treatment with sodium hydrocarbonate. Tetrakis(chelato)dibutoxydititaniumoxanes were obtained by reesterification of hexabutoxydititaniumoxane with acetylacetone and diacetone alcohol in molar ratio 1:4 [4].

Molecular weight of oligomers and polymers were determined by osmometric and viscosimetric methods [5, 6].

The IR spectra of each sample were taken on IR-20 spectrophotometer.

NMR ^{13}C spectra were registered on pulsed Fourier spectrometer NMR EC-567 at operating frequency of 25 MHz, in solution of deuterobenzol. Its resonance lines ^{13}C were utilized as standards.

The thermomechanical curves were taken on a custom-made installation [7]. The test conditions were: $V = 5$ deg/min, $\sigma = 0.1$ kg/cm^2.

Chlorine content was determined by titration method [8]. Hydroxygroups' content was defined by Chugaev-Tserevitinov method [8].

Heterofunctional Polycondensation of α,ω-dihydroxyoligodimethylsiloxanes with tetrakis(chelato) dibutoxydititaniumoxanes

1. 10 g of α,ω-dihydroxyoligodimethylsiloxane (n = 9) were placed in four-necked flask equipped with mixer, reflux condensor, thermometer and nitrogen inlet tube to which a solution of 9.56 g of tetrakis(acetylacetonate) dibutoxydititaniumoxane in 100 ml of anhydrous toluene was added. The reaction mixture was stirred and heated for 1 h after which the solvent was driven off and a sample was taken to measure initial viscosity. The reaction mixture was heated till 180°C and at $P = 1 - 2$ mm Hg under a weak nitrogen flow. In certain time intervals samples have been taken from the reaction mixture to determine viscosity. 18 g (98% of theoretical) of polytetrakis(acetylacetonate)dititaniumoxydimethylsiloxane, a viscous product of orange color were obtained.
2. Similarly, 13.3 g (92% of theoret.) of viscous polymer of orange color was obtained from 10 g of α,ω-dihydroxyoligodimethylsiloxane (n = 17) and 5.1 g of tetrakis(acetylacetonate)dibutoxydititaniumoxane.
3. 33.4 g (98% of theoret.) of elastic light-orange polymer was obtained from 30 g of α,ω-dihydroxyoligodimethylsiloxane (n = 61) and 4.33 g of tetrakis(acetylacetonate)dibutoxydititaniumoxane.
4. 31 g (98% of theoret.) of elastic polymer of yellow color was obtained from 30 g of α,ω-dihydroxyoligodimethylsiloxane (n = 101) and 2.6 g of tetrakis(acetylacetonate)dibutoxy-dititaniumoxane.
5. 103 g (99% of theoret.) of elastic light-orange polymer was obtained from 100 g of α,ω-dihydroxyoligodimethylsiloxane (n = 201) and 4.4 g of tetrakis(acetylacetonate) dibutoxydititaniumoxane.
6. 17.7 g (91% of theoret.) of viscous polymer of orange color was obtained from 10 g of α,ω-dihydroxyoligodimethylsiloxane (n = 9) and 10.5 g of tetrakis(dimethylacetonylcarbinolate)dibutoxydititaniumoxane.
7. 14.3 g (95% of theoret.) of viscous polymer of orange color was obtained from 10 g of α,ω-dihydroxyoligodimethylsiloxane (n = 17) and 5.6 g of tetrakis(dimethylacetonylcarbinolate)-dibutoxydititaniumoxane.
8. 33.4 g (97% of theoret.) of elastic polymer of light-yellow color was obtained from 30 g of α,ω-dihydroxyoligodimethylsiloxane

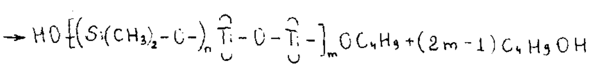
(n = 61) and 6 g of tetrakis(dimethylacetonylcarbinolate)-dibutoxydititaniumoxane.

9. 33.4 g (97% of theoret.) of elastic polymer of light-yellow color was obtained from 30 g of α,ω-dihydroxyoligodimethylsiloxane (n = 101) and 2.92 g of tetrakis(dimethylacetonylcarbinolate)-dibutoxydititaniumoxane.
10. 103.6 g (99% of theoret.) of elastic polymer of light-yellow color was obtained from 100 g of α,ω-dihydroxyoligodimethylsiloxane (n = 201) and 4.82 g of tetrakis(dimethylacetonylcarbinolate)-dibutoxydititaniumoxane.

RESULTS AND DISCUSSION

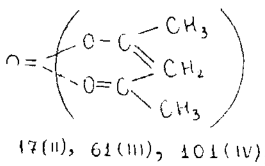
HFC of α,ω-dihydroxyoligodimethylsiloxanes and tetrakis(chelato)-dibutoxydititaniumoxane was conducted in the atmosphere of nitrogen with a molar ratio of initial components 1:1 at the temperature of 180°C. $P = 1 - 2$ mm Hg with simultaneous elimination of butyl alcohol. Reactions were conducted to achieve constant viscosity.

In above mentioned conditions reaction proceeds according to scheme:



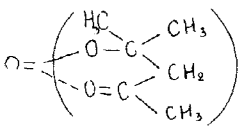
$$m\ HO-[Si(CH_3)_2-O-]_nH + m\ C_4H_9O-\overset{\frown}{\underset{\smile}{Ti}}-O-\overset{\frown}{\underset{\smile}{Ti}}-OC_4H_9 \rightarrow HO\{[Si(CH_3)_2-O-]_n\overset{\frown}{\underset{\smile}{Ti}}-O-\overset{\frown}{\underset{\smile}{Ti}}-]_mOC_4H_9+(2m-1)C_4H_9OH$$

where at



n = 9(I), 17(II), 61(III), 101(IV), 201(V)

and at



n = 9(VI), 17(VII), 61(VIII), 101(IX), 201(X)

Elastic polymers are synthesized using these reactions. Their colors vary from light-yellow to orange. Table I shows their characteristics.

The composition of synthesized polymers is confirmed by IR spectra. Presence of Si—O—Si bonds is accounted for by oscillation in the range 1030–1100 cm^{-1}. Absorption bands in the range 810 cm^{-1} confirm the presence of dimethylsiloxane fragments.

Absorption bands characteristic to Si—O—Ti and Ti—O—Ti bands are superposed on each other in the range 940–970 cm^{-1}.

Presence of acetylacetonate chelate groups in polytetrakis(acetylacetonate)dititaniumoxydimethylsiloxanes is confirmed by oscillations in the range 1600 cm^{-1} characteristic to Ti and C=O coordinate bonds. Absorption band in the range 1545 cm^{-1} confirms the presence of C=C bond, and oscillations in the range 1380 cm^{-1} belong to symmetric deformation bonds of CH_3—groups.

Dimethylacetonylcarbinolate groups in polytetrakis(dimethylacetonylcarbinolate)dititaniumdimethylsiloxanes are characterised by 1620 cm^{-1} oscillations in the range accounted for by C=O bonds,

TABLE I Characterization of poly tetrakis(chelato) dititaniumoxydimethylsiloxanes

Fraction No.	*Elementary composition*[a] *C*	*H*	*Si*	*Ti*	[η], *dl/g*	*M* 10^{-3}	*Yield %*
I	38.71 39.12	6.81 6.93	20.07 19.97	8.60 8.13	0.108	19	98
II	36.53 36.11	7.26 7.40	26.23 25.96	5.62 5.38	0.119	34	92
III	33.84 33.62	7.82 7.56	33.84 33.28	1.93 1.69	0.360	98	98
IV	– –	– –	– –	– –	0.390	130	96
V	– –	– –	– –	– –	0.405	140	99
VI	40.67 40.12	7.80 7.38	18.98 18.54	8.14 8.18	0.111	20	91
VII	37.92 37.83	7.90 7.68	25.28 25.13	5.42 5.39	0.121	36	95
VIII	34.36 34.11	8.04 7.93	33.41 32.96	1.91 1.68	0.380	98	97
IX	– –	– –	– –	– –	0.401	150	97
X	– –	– –	– –	– –	0.428	160	99

[a] In the denominator there are experimental values; in the numerator-calculated values.

and oscillation in the range 1380 and 1470 cm^{-1} accounted for by symmetric deformation oscillations of CH_3—and CH_2—groupings, respectively.

Cis-trans-isomerism of acetylacetonate groups found in dititaniumoxane monomers and polymers by IR spectroscopy was not observed.

When studying NMR spectra of synthesized polymers it turned out that intense signals corresponding to methyl groups at Si atoms overlap the rest part of spectra. However, we think that acetylacetonate groups are in *cis*-position.

In order to determine the rate of polytetrakis(chelato)dititaniumdimethylsiloxanes, synthesis-specific viscosity of polycondensation products in 4% toluene solution was examined over a period of time (Figs. 1, 2).

As figures show, the specific viscosity increases vigorously in first 4 hours and then stops for polymers with a ratio Si:Ti = 9:2 and 17:2.

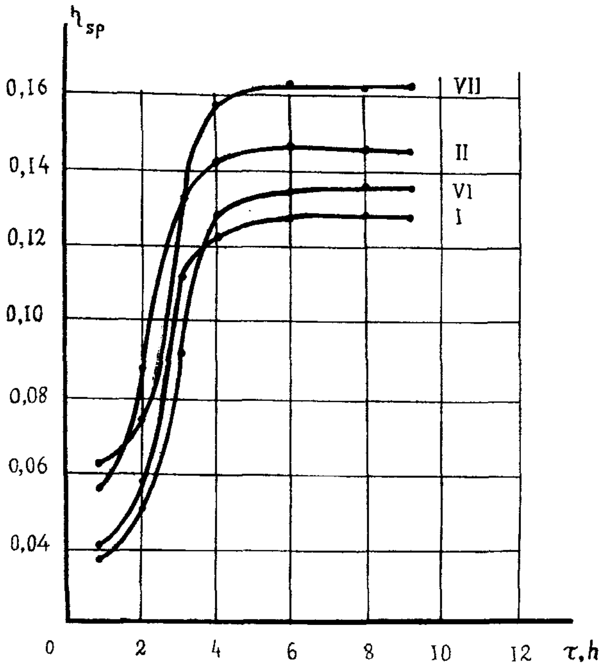


FIGURE 1 Time dependence of specific viscosity of polymer and 4% toluene solution with the molar ratio Si/Ti = 9:2 (I, VI) and 17:2 (II, VII) upon HFC duration.

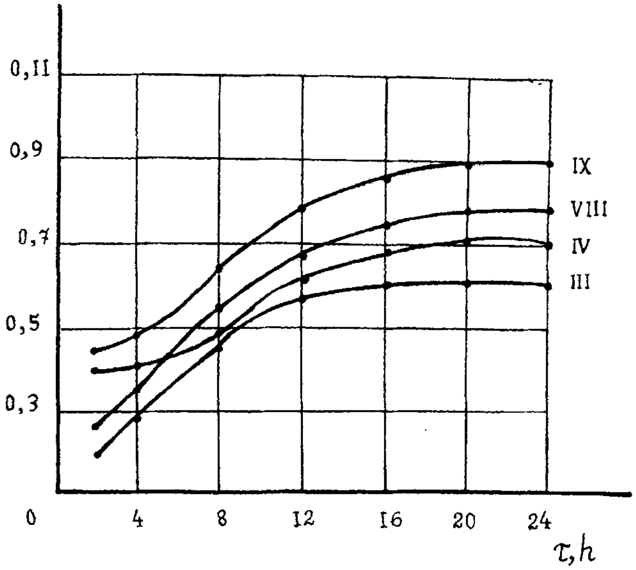


FIGURE 2 Time dependence of specific viscosity of polymers in 4% toluene solution with the molar ratio Si/Ti = 61:2 (III, VIII) and 201:2 (IV, IX) upon HFC duration.

The reaction rate curves of polymers with ratios Si:Ti = 61:2 and 201:2 have a monotonic character, the specific viscosity rises gradually, reaches, its maximum within 20–24 hours of condensation (Fig. 2).

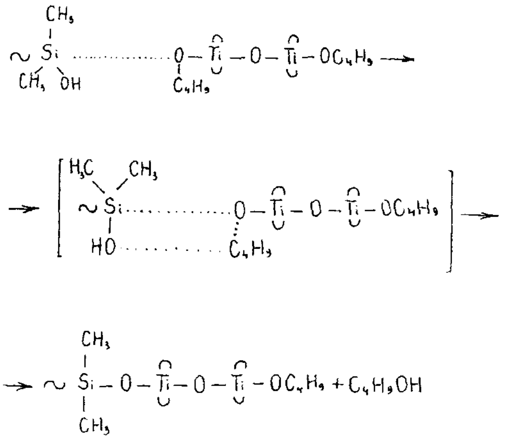
The mechanism of HFC of α,ω-dihydroxyoligodimethylsiloxanes and intramolecular dititaniumoxane compounds can be explained as follows.

Initially coordination of tetrakis(chelato)dibutoxydititaniumoxane butoxyl group oxygen atom with α,ω-dihydroxyoligodimethylsiloxane silicon atom takes place. An intermediate formed during the first stage is then degraded under synthesis conditions with formation of linear polymer and release of butyl alcohol.

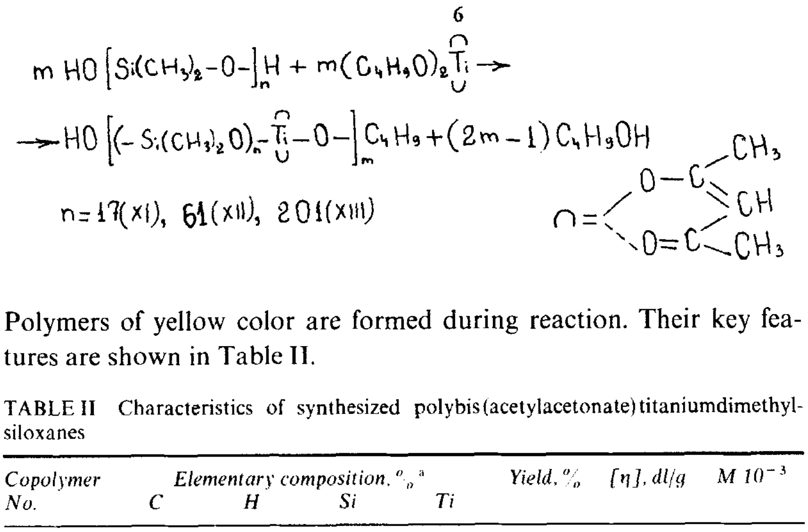
This process proceeds according to the following scheme:

This mechanism is in accordance with those of similar reactions described earlier [9, 10].

In order to compare the obtained polymers with these possessing one Ti atom in main molecular chain we synthesized polybis(acetylacetonate)titaniumdimethylsiloxanes with dimethylsiloxane number: n = 17, 61, 201.



The reaction was conducted according to method [10] under conditions similar to those of polytetrakis(chelato)dititaniumoxydimethylsiloxanes. It proceeds according to scheme:



Polymers of yellow color are formed during reaction. Their key features are shown in Table II.

TABLE II Characteristics of synthesized polybis(acetylacetonate)titaniumdimethylsiloxanes

Copolymer No.	*Elementary composition, %*[a] *C*	*H*	*Si*	*Ti*	*Yield, %*	*[η], dl/g*	*M 10⁻³*
XI	36.14 36.09	7.90 8.20	29.86 29.68	3.01 2.89	96	0.112	32
XII	34.59 34.76	7.75 7.69	35.05 36.10	1.00 1.12	98	0.260	58
XIII	–	–	–	–	99	0.380	138

[a] In the denominator there are experimental values; in the numerator – calculated values.

In order to study influence of dititaniumoxanes and their chelate groups upon polydimethylsiloxane chain we carried out thermomechanical investigations of synthesized polymers.

Experimental data show that polymers containing dititaniumoxane fragments with acetylacetonate chelate groups at n = 17 are characterised by vitrification temperature in the range −113°C and softening at about −10°C.

With the increase of distance between dititaniumoxane fragments, the vitrification temperature decreases to −130°C, and fluidity temperature to −40°C (Fig. 3) in polymers with n = 101.

Thermomechanical curves of polymers with dimethylacetoncarbinolate chelate-groups at dititaniumoxane rings are shown in Figure 4. This figure shows the similar dependence. With the increase of dimethylsiloxanes number between dititaniumoxane rings,

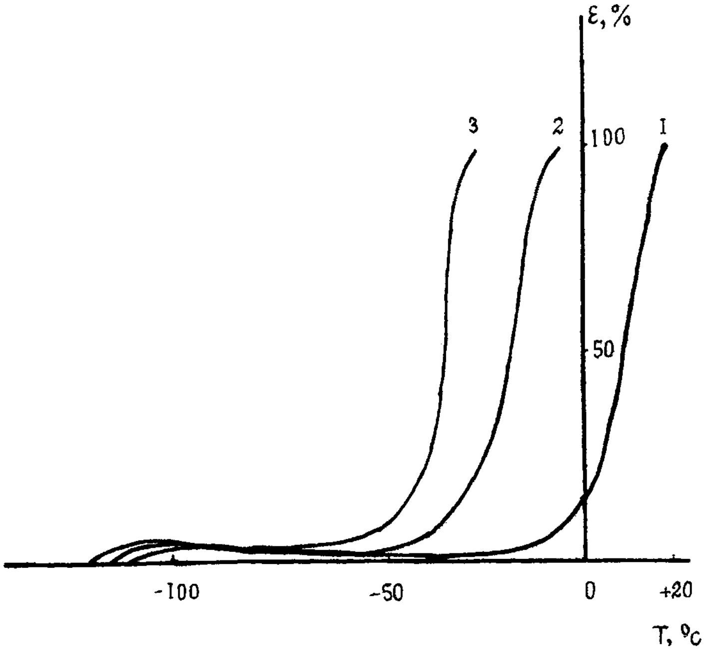


FIGURE 3 Thermomechanical curves of polytetrakis(acetylacetonate)dititaniumoxydimethylsiloxane with the molar ratio Si/Ti = 17:2 (1), 61:2 (2), 101:2 (3).

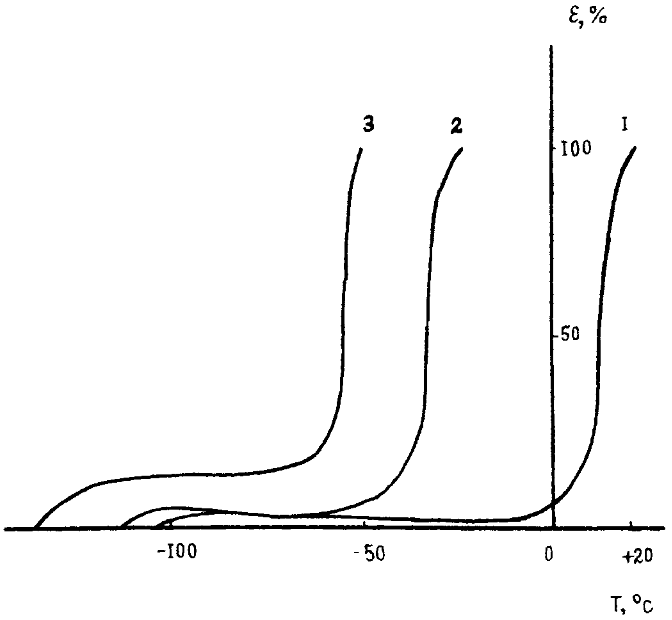


FIGURE 4 Thermomechanical curves of polytetrakis(dimethylacetonylcarbinolate)-dititaniumoxydimethylsiloxane with the molar ratio Si/Ti = 17:2(1), 61:2 (2), 101:2 (3).

the vitrification temperature decreases from −108°C to −138°C. Fluidity temperature is diminished from −10°C to −60°C, respectively.

Such an influence of dititaniumoxane fragments on properties of polydimethylsiloxane chain can be explained by the fact that they are voluminous rigid structures. At small distances polydimethylsiloxane chain acquires increased rigidity. Besides, large sizes of dititaniumoxane fragments make complex packing of molecules difficult and can lead to formation of physical grid that leads to a decrease of vitrification and fluidity temperatures of observed polymers.

In order to compare polymers with one or two titanium atoms in polydimethylsiloxane chain, an investigation of polybis(acetylacetonate)titaniumdimethylsiloxane thermomechanical properties was carried out.

As it is seen on thermomechanical curves of these polymers (Fig. 5), the vitrification and softening temperatures rise from −125°C to 95°C and from −65°C to −40°C, respectively. It is accompanied with

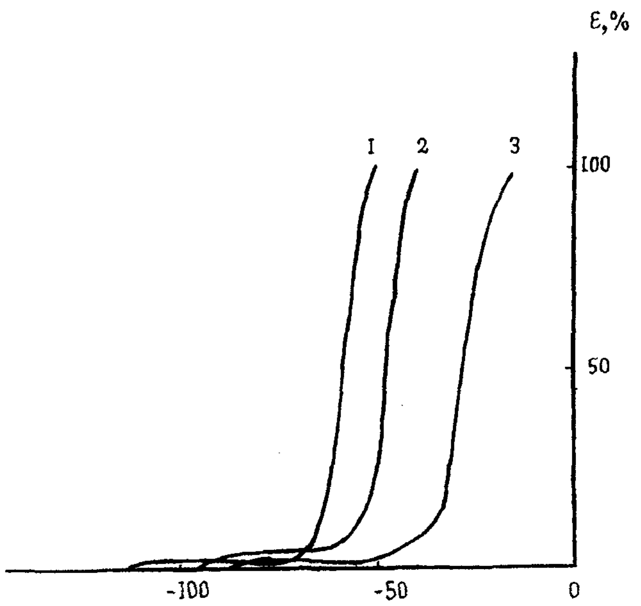


FIGURE 5 Thermomechanical curves of polybis(acetylacetonate)dititaniumoxydimethylsiloxane with the molar ratio Si/Ti = 17:2 (1), 61:2 (2), 101:2 (3).

dimethylsiloxane chain elongation approaching corresponding temperatures of pure dimethylsiloxane.

In support of the rationale that the synthesized high-molecular compounds are copolymers (and not mixture of homopolymers), we carried out an experiment of fractional precipitation of polytetrakis(chelato)dititaniumoxydimethylsiloxane benzene solution. Silicone and Ti atoms, ratio was 9:2. It turned out that all fractions have virtually the same elementary composition (Tab. III), thus providing further support to the fact of copolymer formation.

Figure 6 shows an integral curve indicating distribution of polymer molecular mass. HFC reaction between α,ω-dihydroxyoligodimethylsiloxane ($n = 9$) and tetrakis(acetylacetonate)dibutoxydititaniumoxane results in more significant rate of high-molecular fraction formation compared to that of low-molecular fraction.

The synthesized polymers can be used to impart hydrophobic properties to textile materials and leather.

TABLE III Polytetrakis(acetylacetonate)dititaniumoxydimethylsiloxane fractionation results

Fraction No.	*Elementary Composition* *C*	*H*	*Si*	*Ti*	[η], *dl/g*	*Yield, g*	*Yield, %*
I	39.06	6.96	20.08	8.27	0.108	3.06	29.60
	38.95	6.83	20.06	8.78			
II	38.99	6.59	19.38	8.95	0.093	1.54	14.91
	38.66	6.68	20.05	8.75			
III	38.86	6.82	19.97	8.28	0.086	1.24	12.42
	38.79	6.96	20.07	8.65			
IV	38.72	6.57	20.03	8.38	0.074	0.93	9.01
	38.86	6.68	20.10	8.56			
V	38.65	6.93	20.09	8.35	0.066	2.08	19.62
	38.96	6.75	19.78	8.48			
VI	38.78	6.66	20.13	8.75	0.040	1.49	14.44
	38.54	6.79	20.11	8.68			

Initial copolymers: C 38.71; H 6.81; Si 20. 67; Ti 8.60.

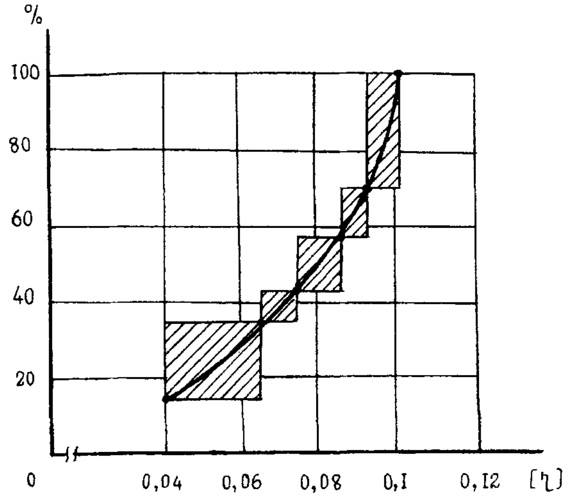


FIGURE 6 Integral curve of polytetrakis(acetylacetonate)dititaniumoxydimethylsiloxane distribution (molar ratio Si/Ti = 9:2) according to molecular masses.

Acknowledgement

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