Condensation Products of the Bifunctionalized Titanocene and Siloxane Derivatives

MARIA CAZACU[1]*, ANGELICA VLAD[1], FELICIA IACOMI[2], PETRU BUDRUGEAC[3], AURELIA IOANID[1]
[1] Petru Poni” Institute of Macromolecular Chemistry Iasi, 41A Aleea Gr. Ghica Voda, 700487, Iasi, Romania
[2] Al. I. Cuza” University, Faculty of Physics, 11 Carol I Blvd., 700506, Iasi, Romania
[3] National Institute for Research and Development in Electrical Engineering ICPE-CA, 313 Splaiul Unirii, 030138, Bucharest Romania

Various telechelic bifunctionalized siloxane derivatives were reacted with titanocene dichloride. The reactant functionality is favorable for the formation of the poly(ester), poly(amine), poly(ether), and poly(silyl-ether) depending on the functional groups of the used siloxane precursors. The interfacial condensation technique was applied and, excepting polyesters, in the other cases, the inverse interfacial system was used. $CHCl_3$ *was used as a solvent for siloxane phase and triethyl amine was added as a hydrochloric acid acceptor. The very fast reactions occurred at room temperature with colour change from red-orange to yellow. The poly(ester) was also synthesized in solution by using DMF as a solvent. The formation of new structures was verified by FTIR and their thermal behaviour was investigated by TGA and DSC. SEM and Energy Dispersive X-Ray system (EDX) were used to show the morphology of the poly(ether). The repartition of Ti was investigated by EPR.*

Keywords: siloxane-titanocene copolymers; polycondensation; metallocene; siloxane

The polymers containing metallocene in the main chain are of high interest as catalysts, especially stereoregular catalysts. There are also a number of other potential uses including corrosion resistant coatings, thermally stable materials, liquid crystals (some metallocene derivatives possessing mesogenic properties), electrodes, laser interactions, high strength nanofibers, semiconductors, sensors, solar energy conversion or in control-release applications [1]. Metallocenium radicals are fundamental building blocks in ferromagnetic materials and precursors for charge transfer complexes [2]. Metallocene-based compounds often display unexpected biological activity that resulted in their wide application in pharmacy (manufacture of anticancer and antimalarial drugs, and radiopharmaceutical agents), biochemistry (biosensors for DNA detection), etc. [3].

In our previous papers [4,5] we reported the synthesis of some condensation polymers (polyesters, polyamides, polyester-azomethines and polysilylesters) of ferrocene, siloxane derivative being the co-monomer sequence.

In the present work we synthesized some polycondensation compounds containing titanocene according to the procedure reported in literature. Metallocenes-containing polyamines, polyethers, polythioethers and polyesters of group IVB [1] starting from a metallocene with the general formula Cp_2MXY (where X and Y can be any of the halides, hydrogen, alkyl and aryl groups) and a proper organic partner: diamine, diol, ditiol, and dicarboxylic acid salt were synthesized. We used various siloxane derivatives instead of organic compounds. Polysiloxanes were already used as support materials for metallocene catalysts. Poly(methylsiloxane) was reacted with 1,1'-allyl-substituted cyclopentadienyl zirconium dichloride. Hydrosilylation catalyzed by H_2PtCl_6 of the double bonds of the allyl groups with the Si-H bonds of the polysiloxane resulted in zirconocene covalently bonded to the polysiloxane chains [6]. Polysiloxane microgel functionalized with chlorosilanes containing fluorenyl groups was reacted with $(\eta_5\text{-}C_5Me_5)ZrCl_3$ or $ZrCl_4$ to produce the polysiloxane-micro-gel-supported zirconocene compounds [7].

It would be expected that the presence of siloxane would improve solubility and would decrease the transition temperatures of the resulted polymers and confer them ability to form films. Cp_2TiCl_2 was chosen as the titanocene moiety provider. The presence of ester, amine or ether internal functions would also influence most of the copolymer behaviors (thermal, mesomorphic, photochemical and redox). Thus, the type of bond between the two co-monomer units can be used as a parameter in designing compounds with desired properties. Therefore, the polycondensation procedure is preferred for the synthesis of such compounds. In addition, this procedure permits to use a large range of functionalized monomers. Model compounds can be obtained in order to characterize and understand the behaviour of polymers.

The paper originality consists in the structures obtained by using siloxane derivatives besides titanocene.

Experimental part

Materials

Dicyclopentadienyltitanium dichloride, Cp_2TiCl_2 (Fluka) was used as received.

1,3-Bis(aminopropyl)tetramethyldisiloxane, (AP_0), supplied by Fluka was used as received.

1,3-Bis(hydroxybutyl)tetramethyldisiloxane (HB_0) supplied by Fluka, b.p. 148, $d_4^{20}=0,93$ was used as received.

1,3-Bis(3-carboxypropyl)tetramethyldisiloxane, $(HOOC(CH_2)_3(CH_3)_2Si)_2O$, CX, was prepared by hydrolysis of 1,3-bis(cyanopropyl)tetramethyldisiloxane [8] (84% yield): m. p. = 50 °C.

Diphenylsilanediol, $(C_6H_5)_2Si(OH)_2$, DFSD, was prepared by hydrolysis of diphenyldichlorosilane in diethylether/water or acetone/water mixture, in the presence of an anion exchanger having weakly basic groups as hydrochloric

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* email: mcazacu@icmpp.ro

acid acceptor. The product (recrystallized from benzene) with m.p. = 148-151°C was obtained in 87% yield.

Triethylamine, TEA (Fluka) was used as received.

Solvents: DMF (Fluka) and chloroform (Chimopar) were freshly dried before using.

Equipment

FTIR absorption spectra were recorded from KBr pellets on a FT-IR Vertex 70 (Bruker, Germany).

Electronic absorption spectra were measured using SPECORD M42 spectrophotometer with quartz cells of 1 cm thickness in different solvents.

Thermogravimetric measurements were performed with an STA 490C apparatus manufactured by Netzsch-Germany, in static air atmosphere, in the temperature range 25 ÷ 1000^0C, and a heating rate of 10 K.min^{-1}. The DSC traces were also recorded using a DSC 204F1 Phoenix apparatus manufactured by Netzsch-Germany in the following conditions: the temperature program: $20^0\mathrm{C} \rightarrow -80^0\mathrm{C}$ – isotherm 20 min $\rightarrow -80^0\mathrm{C} \xrightarrow{10\mathrm{K/min}} 150^0\mathrm{C}$; in Ar (purity 99.999%) flow (20mL . min^{-1}); aluminum crucible. The glass transition temperature was determined as the midpoint of the heat capacity change in the heating scan. DSC scans on the temperature range -150 ÷ -40°C were performed at a heating rate of 20° C/min with a Pyris Diamond DSC, power compensated differential calorimeter type from Perkin Elmer, USA.

Microscopic investigation was performed on an Environmental Scanning Electron Microscope (ESEM) type Quanta 200 operating at 20kV with backscattered electrons in low vacuum mode. The coupled Energy Dispersive X-Ray system (EDX) permitted to perform the qualitative and quantitative analysis and elemental mapping.

Electron paramagnetic resonance (EPR) spectra of the samples was registered at room temperature by using Spectrometer ADANI, in X band.

Procedures

Synthesis of the polyester PEST1 (procedure I)

1 mmol (0.306g) of 1,3-Bis(carboxypropyl)tetramethyl disiloxane was suspended in 25 mL water. A solution of 0.1N KOH was added in the presence of phenolphtaleine until a homogeneous solution having a stable pink colour was formed. This solution was added by a dropping funnel to the solution containing 1 mmol titanocene dissolved in 25 ml chloroform under stirring. The colour of the reaction mixture stepwisely changed from red to yellow. The stirring was continued for another 15 min after which two layers separated: colorless water upper layer and yellow organic lower layer. The organic layer was isolated and repeatedly washed by mixing with water, dried with Na_2SO_4 and the solvent was removed in vacuum. The yellow-orange solid remained as a film and became insoluble in common organic solvents.

Synthesis of the polyester PEST2 (procedure II)

The potassium salt of 1,3-bis(3-carboxypropyl) tetramethyldisiloxane, CxK, prepared as above described, was isolated by precipitation of the concentrated aqueous solution in acetone, filtering and drying in vacuum. The mixture consisting in 1 mmol (0.382 g) of CxK and 1mmol (0.249g) of Cp_2TiCl_2 dissolved together in 10 mL freshly dried DMF was stirred at 100°C under nitrogen atmosphere for about 12 h. The colour of the reaction mixture changed from orange to yellow and a precipitate appeared. Then, the mixture was filtered to separate NaCl. The filtrate was precipitated in a large excess of water. The reaction product was isolated as precipitate by filtration, washing with water and acetone and drying.

Synthesis of the polyether, PET and polyamine, PAT

A solution consisting in 1 mmol (0.249g) of Cp_2TiCl_2 dissolved in 25 mL water was added by means of a dropping funnel to a solution containing 1 mmol of bifunctionalized siloxane (0.248g AP_0 or 0.278g HB_0) and 2 mmol of TEA dissolved in 25 mL of chloroform under stirring. The colour of the solution quickly changed from red-orange to yellow. A light yellow precipitate formed concomitantly. The mixture was stirred for another 15 min and then was filtered. The precipitate was washed with chloroform and dried under vacuum at 100°C, proving to be triethylamine chlorohydrate. The organic fraction of the biphasic filtrate was separated and repeatedly washed with water, dried on Na_2SO_4 and the solvent was removed in vacuum. The remained yellow solid was insoluble in common organic solvents.

Synthesis of the poly(silyl-ether), PSiT

1mmol (0.216) of diphenylsilanediol was suspended in 20 mL $CHCl_3$. Acetone (5 mL) was added in order to completely dissolve it. 2mmole of TEA were also added. A solution consisting in 1 mmol (0.249g) of Cp_2TiCl_2 solved in 25 mL water was added by a dropping funnel to the above prepared mixture under stirring. After reaction occurrence the mixture was processed as in the case of polyamines and polyethers. A brittle yellow-orange transparent film was formed. This is soluble in DMF, DMSO, NMP, $CHCl_3$, acetone, CH_2Cl_2 and insoluble in methanol, ethanol, THF.

Depending on the used alkylation agent, an acid (in our case HCl) is formed as by-product in such a reaction that usually is trapped by a base added in the reaction medium.

Results and discussion

A series of condensation products of titanocene dichloride with various siloxane derivatives have been prepared. Because all precursors are bifunctional reactive reagents and are used in stoichiometric amounts there are conditions to form polymers: poly(ester), poly(amine), poly(ether), and poly(silyl-ether) depending on the functional groups of the siloxane precursors (scheme 1). The interfacial polycondensation technique was applied and, excepting polyesters, in all other cases the inverse interfacial system was used. This is because the siloxane components are not soluble in water. $CHCl_3$ was used as a solvent for organic phase and triethyl amine as a hydrochloric acid acceptor. When a siloxane diacid is converted in salt, this could be dissolved in aqueous phase and direct interfacial system can be used. The reactions occurred very fast at room temperature with color changing from red-orange to yellow. TEA was used as an effective HCl acceptor. It is easily removable since both TEA and TEA·HCl are soluble in water. It has also been shown that TEA does not compete with diol or diamine in reaction with M-Cl site, presumably because of its steric hindrance [9].

It has been ascertained that the polymers are soluble in organic phase remained in solution. However, after solvent removing the polymers, excepting the poly(silyl-ether), became insoluble in common organic solvents. Poly(silyl ether), PSiT, derived from the titanocene and diphenilsilanediol is soluble in DMF, DMSO, NMP, $CHCl_3$, acetone, CH_2Cl_2 and insoluble in methanol and ethanol. The presence of the phenyl substituents in PSiT impedes packing of the chains and as a result the product is soluble.

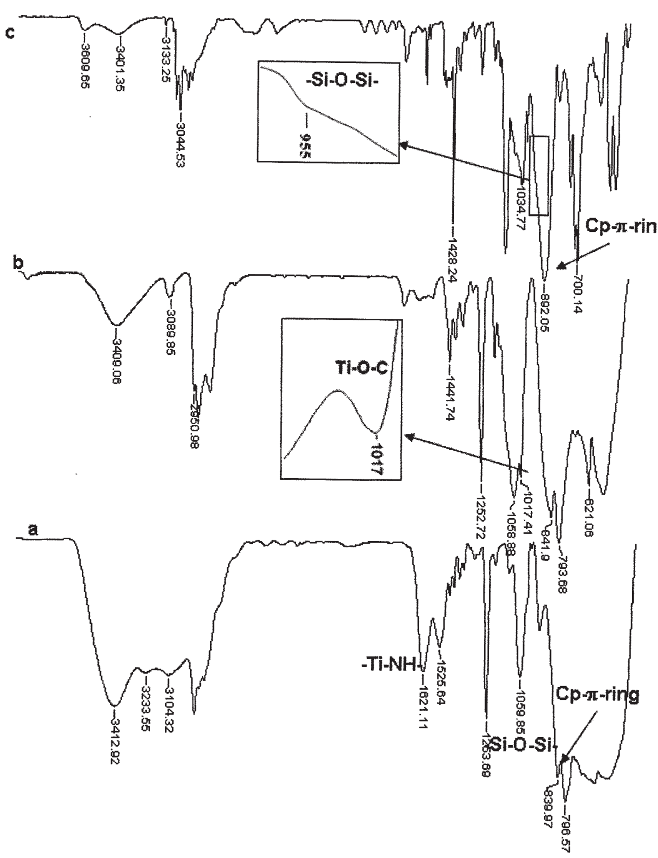


Fig. 1. FT IR spectra for: a - poly(amine)-PAT; b - poly(ether)-PET; c-and poly(silyl-ether)-PSiT

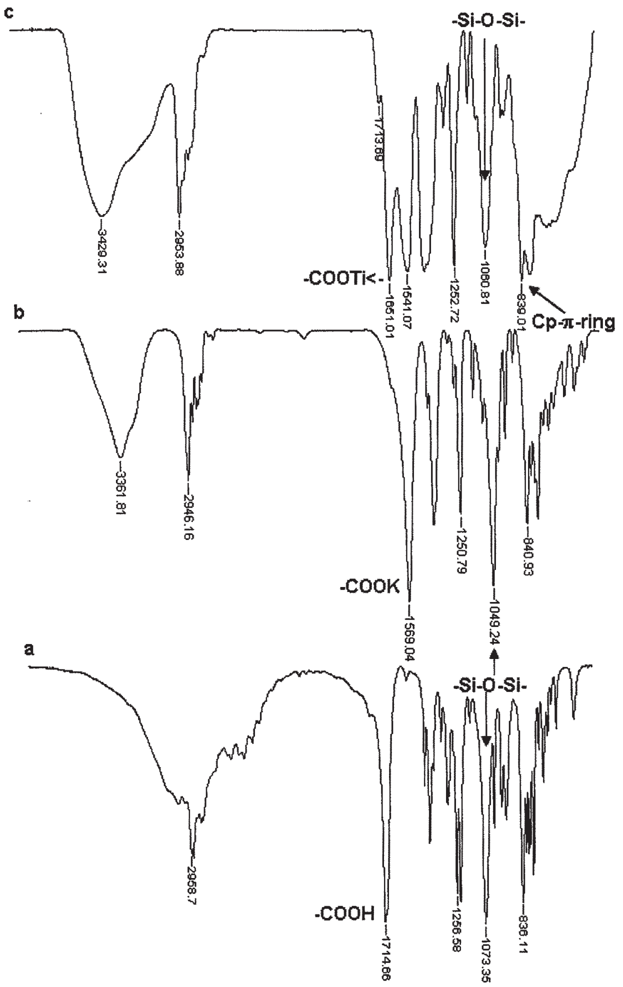
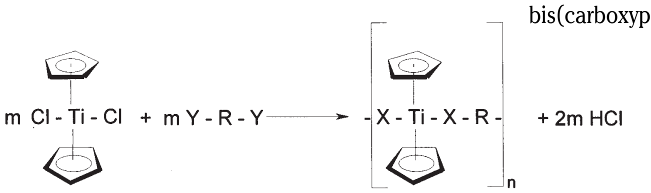
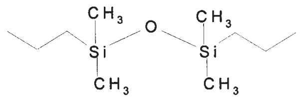
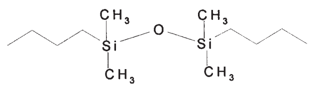


Fig. 2. FT IR spectra for 1,3-bis(carboxypropyl)tetramethyldisiloxane (a), dipotasic salt (b), and polyester PEST2 (c)



Sample	Polymer type	Y	X	R	Procedure
PAT1	Poly(amine)	NH_2	NH		I. I. P.[a]
PEST1	Poly(ester)	COO^-K^+	COO		D. I. P.[b]
PEST2					S. P.[c]
PET1	Poly(ether)	(C-)OH	O		I. I. P.[a]
PSiT	Poly(silyl-ether)	(Si-)OH	O	$(C_6H_5)_2Si<$	I. I. P.[a]

[a]Inverse interfacial polycondensation; [b]Direct interfacial polycondensation; [c]Solution polycondensation.

Scheme 1

The specific absorption bands developed in FTIR spectra for the products were used as main tool for the structure confirmation (figs. 1, 2).

During synthesis procedure, the rapid formation of the triethylamine chlorohydrate has been observed in all cases, this being a first sign that the reaction occurs. The formation of the titanocene-siloxane structures was verified by FTIR following mainly the presence of the newly formed linkages between siloxane and titanocene moieties.

Formation of the polyamine is supported mainly by the dissapearance of the N-H stretching bands at 3302 and 3360 cm^{-1} in the primary diamine precursor and the development of a new band at 3233 cm^{-1}, characteristic for the secondary amine. In addition, the N-H deformation

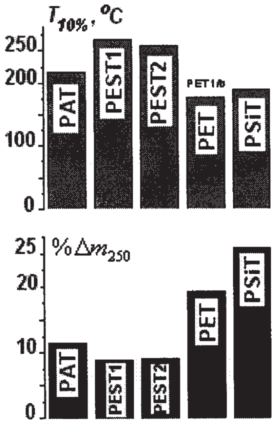


Fig. 3. $T_{10\%}$ and Δm_{250} values for the prepared titanocene-siloxane copolymers

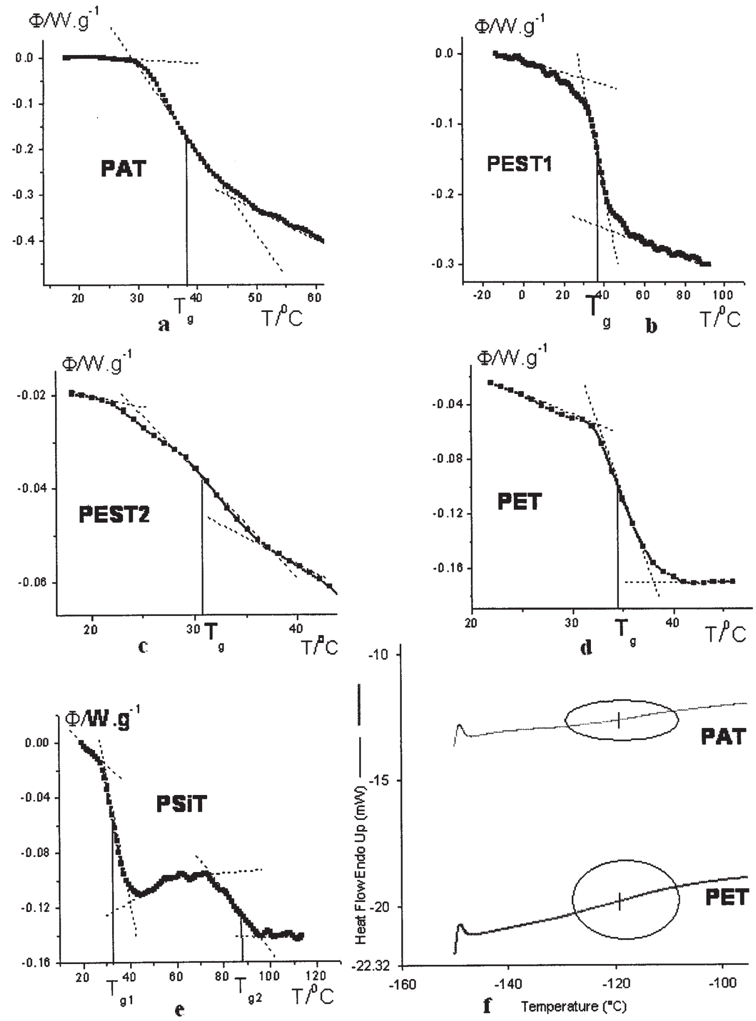


Fig. 4. DSC traces of the titanocene-siloxane condensation products

Table 1
THE MAIN PARAMETERS OF DSC CURVES

Sample	$T_{initial}$ °C	T_{final} °C	T_g °C	ΔC_P J.g^{-1}.K^{-1}
PAT	31.1	43.0	37.4	1.665
PEST1	33.3	43.8	37.1	1.133
PEST2	26.1	33.9	30.9	0.152
PET	32.4	38.1	34.0	0.693
PSiT	28.1	38.5	31.4	0.563
	75.4	94.1	89.0	0.293

T_g = glass transition temperature; ΔC_P = specific heat variation.

vibrations are shifted from 1575 and 1485 cm^{-1} in starting amine to 1621 and 1526 cm^{-1}, in the reaction product (fig.1a) [10]. The presumed structure is also confirmed by the presence of the other bands characteristic for titanocene or siloxane moieties: 3401 cm^{-1} (OH); 3104 (C-H stretching in π-Cp groups); 2954 C-H; 1468 (Cp-π-ring); 1408 (CH_3); 1253 (Si-CH_3); 1060 (Si-O-Si); 839 cm^{-1} (Cp-π-ring); 796 (Si-CH_3).

In the spectrum of the product of the reaction between Cp_2TiCl_2 and HB_0 (PET), the band at 1020 cm^{-1}, assigned to newly formed Ti-O-C bond [11], can be identified besides the bands characteristic for the cyclopentadienyl and siloxane moieties : 3421 cm^{-1} (OH); 3103 (C-H stretching in π-Cp groups); 2926 C-H; 1441 (Cp-π-ring); 1407 (CH_3); 1252 (Si-CH_3); 1056 (Si-O-Si); 842 cm^{-1} (Cp-π-ring), 795 (Si-CH_3) (fig. 1b).

As a result of the reaction between Cp_2TiCl_2 and DFSD, the Ti-O-Si bond is formed in PSiT, which is confirmed by the shoulder at 955 cm^{-1} [12,13]. However, diphenylsiloxane sequences also formed as the presence of the band at 1034 cm^{-1} suggests [14]. There are also present the bands: 3609 (aromatic-OH); 3419 cm^{-1} (H_2O); 3133 cm^{-1} (C-H stretching in π-Cp groups); 3065, 3044 cm^{-1} (aromatic C-H); 1428 cm^{-1} (Cp-π-ring); 892 cm^{-1} (Cp-π-ring), 700 cm^{-1} (Si-C_6H_5); 512, 473 cm^{-1} (aromatic ring) (fig. 1c).

The formation of CxK salt was also emphasized by FTIR where the band at 1714 cm^{-1} assigned to COOH groups (fig. 2a) disappeared and a new band at 1569 cm^{-1} is

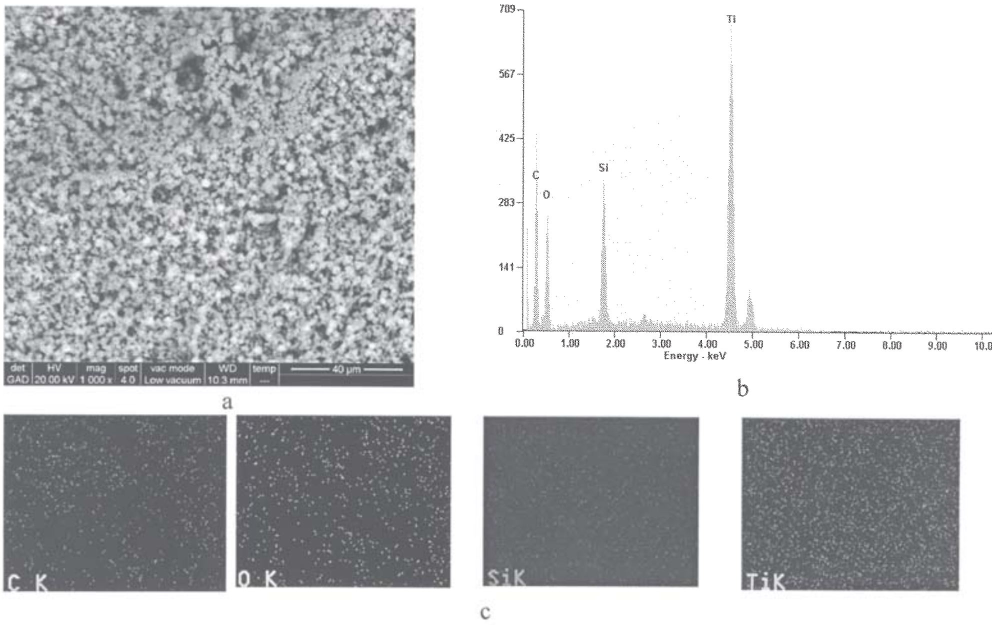


Fig. 5. SEM image and EDX results for the sample PET

Table 2

COMPARISON BETWEEN THE CALCULATED ELEMENTAL COMPOSITION AND THAT FOUND BY EDX FOR THE SAMPLE PET

Element	**Wt.%**		**Atom %**	
	Calculated[a]	**Found by EDX**	**Calculated**[a]	**Found by EDX**
Ti	12.0	24.0	3.7	8.4
Si	14.0	5.9	7.4	3.4
C	66.0	44.2	81.5	61.3
O	8.0	25.9	7.4	27.0

[a] Based on the presumed structural unit: $-Cp_2Ti-O-(CH_2)_4-(CH_3)_2Si-O-Si(CH_3)_2-(CH_2)_4-O-$

developed as a result of the formation of COOK group (fig. 2b). In the spectrum of the condensation product of CxK salt with Cp_2TiCl_2 was identified the presence of -Ti-OCO-group by the band at 1651 cm^{-1} (fig. 2c). Other interesting spectral bands: 3421 cm^{-1} (OH); 3120 cm^{-1} (C-H stretching in π-Cp groups); 2953 cm^{-1} (C-H); 1713 cm^{-1} (residual -COOH); 1436 cm^{-1} (Cp-π-ring); 1407 cm^{-1} (CH_3); 1252 cm^{-1} (Si-CH_3); 1060 cm^{-1} (Si-O-Si); 839 cm^{-1} (Cp-π-ring); 794 cm^{-1} (Si-CH_3). Based on the ratio between carboxyl and ester groups, the polyester PEST2 obtained by procedure II seems to have a molecular weight higher as compared with PEST1 where the band assigned to carboxyl group has low intensity.

In order to evaluate the thermal stability of the investigated products, the following parameters have been determined from the thermograms: $T_{x\%}$ - temperature assigned to x% (x%=10%) and %Δm_T- mass loss at temperature T (T = 250°C). The decreasing order of $T_{x\%}$ and increasing order of %Δm_T is considered the order of thermal stability decreasing order [15-17]. In figure 3 are graphically presented the $\boldsymbol{T_{10\%}}$ and %Δm_{250} values for investigated samples. It can be noticed that the polyesters PEST1 and PEST2 show highest thermal stabilities.

The compounds expected to result from the described procedures are segmented copolymers. PAT, PEST1, PEST2, and PET would consist in disiloxane-aliphatic sequences containing nine or eleven co-chained atoms (C_3-Si-O-Si-C_3 or C_4-Si-O-Si-C_4) alternating with titanocene units. The joints between the two sequence types are: Ti-NH-C-, Ti-OOC-, Ti-O-C, Ti-O-Si-. According to [18], short units like titanocene are considered to act only as a chain extender [polyA-X]x. There is the opinion that the segments X, which forms the junctions between blocks, may bring interesting properties but generally phase separation does not occur [18]. DSC analyses performed in the temperature range –80 ÷ +150°C emphasize Tg values in the positive domain (fig. 4a-e, table 1). The presence of Tg in the positive temperature range in a compound containing high flexible siloxane sequences leads to the idea that probably there is also an additional Tg around -120°C assigned to the siloxane domains as we find in the case of the similar copolymers containing short organic moieties instead of titanocene where phase separation was proved [19]. Indeed, on the DSC curves recorded for the samples PAT and PET (fig. 4) in the low temperature range, glass transition temperatures at about -120°C can be identified (fig. 4f). Although such behaviour is somehow strange because the copolymers' sequences are too short to form domains that would show transition temperatures, many other evidences were subsequently found for this [20,21]. An explanation would be the high flexibility of the siloxane that permits the self-assembly of the copolymer sequences in aggregates by either polar or nonpolar interactions. In the case of PSiT sample, the siloxane sequence is diphenyl-substituted one that generally shows transition in the positive range. Therefore, the transition assigned to the organometallic (89 °C) as well as that assigned to siloxane (31.4 °C) are visible in the approached temperature domain [22]. The formation of the siloxane sequence in PSiT was already emphasized in FTIR spectrum (fig. 1d). SEM investigation of the PET sample revealed a structuration of the material

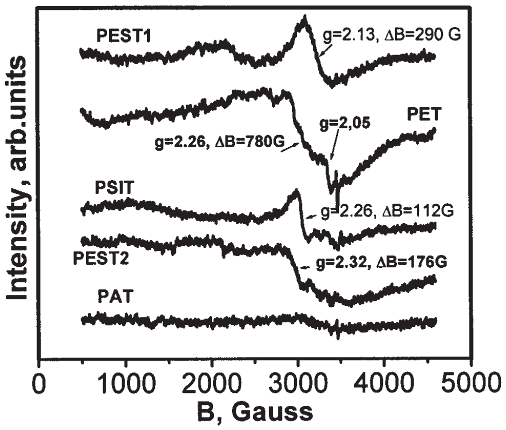


Fig. 6. Second derivative of Ti^{3+} EPR spectra of studied samples, registered at room temperature (Spectrometer ADANI, X band)

in spherical particles having average diameter around 1μ. The image taken with backscattered electrons to obtain compositional contrast (fig. 5a) shows light particles suggesting the presence of the titanium on the surface. The EDX method that provides the X-ray elemental distribution spectrum (fig. 5b) at a depth of 100-1000 nm confirms this by higher titanium content as compared with that calculated on the idealized structure basis, while the other elements were found in lower masic and atomic contents as compared with calculated ones (table 2). A core-shell morphology with shell consisting mainly in titanium units would explain these results. The elemental distribution mapping within the investigated portion is presented in figure 5c.

The registered EPR spectra exhibit different EPR signals belonging to Ti^{3+}: monomeric dimeric and polymeric species (fig. 6). Their distribution is specific for every compound being influenced by the nature of the neighbourhoods. A broad signal is a proof for the presence of many neighbourhood types.

Conclusion

The condensation of the titanocene dichloride with various silicon derivatives [1,3-bis(3-aminopropyl) tetramethyldisiloxane, 1,3-bis(carboxypropyl) tetramethyldisiloxane, 1,3-bis(hydroxybutyl) tetramethyldisiloxane and diphenylsilanediol] lead to the products having different internal functions [-Ti-NH-,- Ti-COO-, -Ti-O-(C), -Ti - O - (Si)-] as FTIR spectra evidenced by the presence of the specific absorption bands. Excepting poly(silyl-ether)s, in general the resulted polymers were insoluble. The thermal stability depended on the internal groups, the most stable proving to be polyesters. DSC, SEM and EDX results suggested the formation of biphasic morphology. The EPR spectra evidenced the existence of the Ti^{3+} species that are known to be suitable for catalysis.

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