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Influence of ethylene glycol on the hydrolysis-condensation behavior of Ti(IV) butoxide

St. I. Yordanov[1], A. D. Bachvarova-Nedelcheva[2*], R. S. Iordanova[2]

[1] Institute of Metal Science, equipment, and technologies "Acad. A. Balevski" with Center for Hydro- and Aerodynamics at the Bulgarian Academy of Sciences, 67 "Shipchenski prohod" str., 1574 Sofia, Bulgaria
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev", bl. 11, 1113 Sofia, Bulgaria

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

This study is aiming to verify the influence of ethylene glycol (EG) on the degree of hydrolysis – condensation reactions during the sol – gel processing and obtaining of pure titania gels. Two homogeneous gels were obtained using titanium (IV) butoxide with and without addition of EG and presence only of air moisture. By XRD was established that the gel prepared without addition of EG (TBT) is amorphous up to 300 °C while the other one (TBT/EG) is amorphous even at 400 °C. It is found that TiO_2 (anatase) is a dominating crystalline phase during the heating up to 600 °C while at 700 °C, TiO_2 (rutile) appeared. The IR and UV-Vis analyses revealed a completeness of hydrolysis – condensation reactions in the TBT/EG in comparison to pure TBT gel. The UV-Vis spectra of TBT/EG gel exhibited a red shift of the cut-off compared to pure TBT one.

Key words: sol-gel; phase transformations; IR spectra; UV-Vis spectra

INTRODUCTION

The sol–gel derived titanium dioxide nanoparticles are of great interest for many applications. Among different precursors the Ti(IV) n-butoxide is widely used for nanopowders (nanowires, nanotubes, etc.) and films preparation [1, 2]. It is well known that the chemistry of sol–gel process is mainly based on hydrolysis and polycondensation reactions leading to formation of a polymerized oxide network. The systematically studies during the last 20 years aimed to examine the processing parameters that control the degree of hydrolysis – condensation reactions. Some excellent reviews are devoted to this topic [3-6]. The high reactivity of metal alkoxides towards water leads to complex hydrolysis and polymerization reactions. Generally, the hydrolysis reaction is influenced by a number of factors such as nature of the alkyl (R) group, the nature of the solvent, the concentration of the species present in solution, the water to alkoxide molar ratio and the temperature [7,8,9]. Depending on the chemical conditions, very different structures can be obtained ranging from colloidal particles to precipitation or gels. The mechanisms of these reactions have been extensively studied in the case of silicon alkoxides, whereas much less data are available for transition – metal oxide precursors [10]. It was found that the titania sol–gel process follows essentially a different pathway than the silicon based one [1]. According to Brinker and Sherer [11] the metal alkoxides, especially those of the early transition metals (Ti, Zr) possess lower electronegativity that causes them lower stability toward hydrolysis and condensation. The greater reactivity of these alkoxides requires that they be processed with stricter control of moisture and conditions of hydrolysis in order to prepare homogeneous gels rather than precipitates. The above mentioned is the main reason for the fundamental studies of hydrolysis and condensation of transition metal alkoxides [1,11-13].

Our team has experience on the sol-gel obtaining of powders in different binary and multicomponent systems where Ti(IV) butoxide is used as a main precursor [14-17]. During the structural characterization of these samples some questions arose related to the completeness of the hydrolysis-condensation processes and their dependence on the nature of the dissolvent and temperature. This motivated our research in this direction.

The present paper aiming to verify the influence of ethylene glycol (EG) on the hydrolysis - condensation behavior of Ti(IV) n-butoxide during the sol – gel process and obtaining of pure titania powders. Moreover, the experiments have been

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* To whom all correspondence should be sent:
E-mail: *albenadb@svr.igic.bas.bg*

performed without addition of water in order to prevent the non – equilibrium fast hydrolysis of Ti butoxide. A comparison of the phase formation and short range order of the obtained gels and powders is made as well.

EXPERIMENTAL

Preparation of the gels

Two gels were prepared using Ti(IV) n - butoxide without direct addition of water and the sol-gel hydrolysis reaction was accomplished only in presence of air moisture. One of the gels was obtained without usage of ethylene glycol (EG) as a dissolvent while the other one was prepared by dissolving the Ti butoxide in EG (in 1:1 molar ratio), denoted as TBT and TBT/EG, respectively. According to the literature data [18,19], the using of diols as solvents is preferable due to their ability to modify the metal alkoxides and to act as chelating ligands forming bridges with other alkoxide groups. By this way, the obtained solutions become sufficiently stable. The pH of as-prepared solutions was measured 4-5. The aging of TBT and TBT/EG gels was performed in air for several days in order to allow further hydrolysis. After that they were subjected to the stepwise heating in air up to 700 °C for one hour exposure time for each temperature. In the temperature range 150-200 °C the bulk samples are broken into small pieces during the drying. Further increasing of temperatures (300-700 ^{o}C) was important to verify the phase transformations of the gels.

Samples characterization

Powder XRD patterns were registered at room temperature with a Bruker D8 Advance diffractometer using Cu-K_{α} radiation. The infrared spectra were registered in the range 1600-400 cm^{-1} using the KBr pellet technique on a Nicolet-320 FTIR spectrometer with 64 scans and a resolution of ±1 cm^{-1}. The optical absorption spectra of the powdered samples in the wavelength range 200–1000 nm were recorded by a UV–Vis diffused reflectance spectrophotometer "Evolution 300" using a magnesium oxide reflectance standard as the baseline.

RESULTS AND DISCUSSION

Phase transformations

Transparent and monolithic gels were obtained. The XRD patterns of samples heat treated in the temperature range 200-700 °C are shown in Fig. 1. As it is seen in both samples (TBT and TBT/EG) the amorphous phase is dominant up to 300 °C. At 400 °C in the XRD pattern of TBT first crystals of TiO_2 (anatase) (JCPDS 78-2486) are registered, while the TBT/EG sample is still amorphous due to the higher amount of organics as a result of the addition of EG. Thus, the presence of organic groups from the dissolvent led to stabilization of the amorphous state at higher temperatures. In the temperature range 500-600 ^{o}C powders containing only crystalline TiO_2 (anatase) are observed. The increasing of temperature (700 °C) led to the appearance of TiO_2 (rutile) (JCPDS 21-1276). It is worth noting that in the XRD pattern of sample TBT/EG the anatase to rutile phase transformation is more completed (Fig. 1). At 500 ^{o}C the average crystallite size (calculated using Sherrer's equation) of TiO_2 (anatase) in the TBT and TBT/EG samples is 12 and 5 nm, respectively (Fig. 1). At higher temperature (600 ^{o}C) the crystallite size increased and it is about 16 nm in both samples.

UV - Vis spectroscopy

The UV-Vis spectroscopy is applied in order to obtain information for the completeness of the hydrolysis – condensation reactions. The diffuse reflectance absorption spectra of both gels (aged at room temperature) and heated at 200 °C are shown in Fig. 2.

As one can see from the figure, the UV-Vis spectra of TBT and TBT/EG gels are characterized by two bands 240-250 nm and 320-340 nm. It is known, that the main building units in the unhydrolyzed Ti butoxide are isolated TiO_4 groups with absorption band in the region 240-260 nm. As a result of the polymerization processes TiO_4 groups are transformed into TiO_6 units possessing absorption about 320-340 nm [20-22]. Looking at our spectra some differences could be distinguished. It is obvious that in the spectra of TBT/EG gel the band at 320-340 nm is more intensive as compared to 240-250 nm. That is associated with an increase of the polymerization degree of Ti atoms in comparison to pure TBT gel. This experimental fact could be explained by the presence of ethylene glycol. The heating at 200 °C led to the further transformation of TiO_4 to TiO_6 units and higher degree of polymerization processes, respectively. The other difference is the shifting toward higher wavelengths (340 nm) in the spectra of heated at 200 °C TBT and TBT/EG samples that could be related with the increasing number of reaction intermediates.

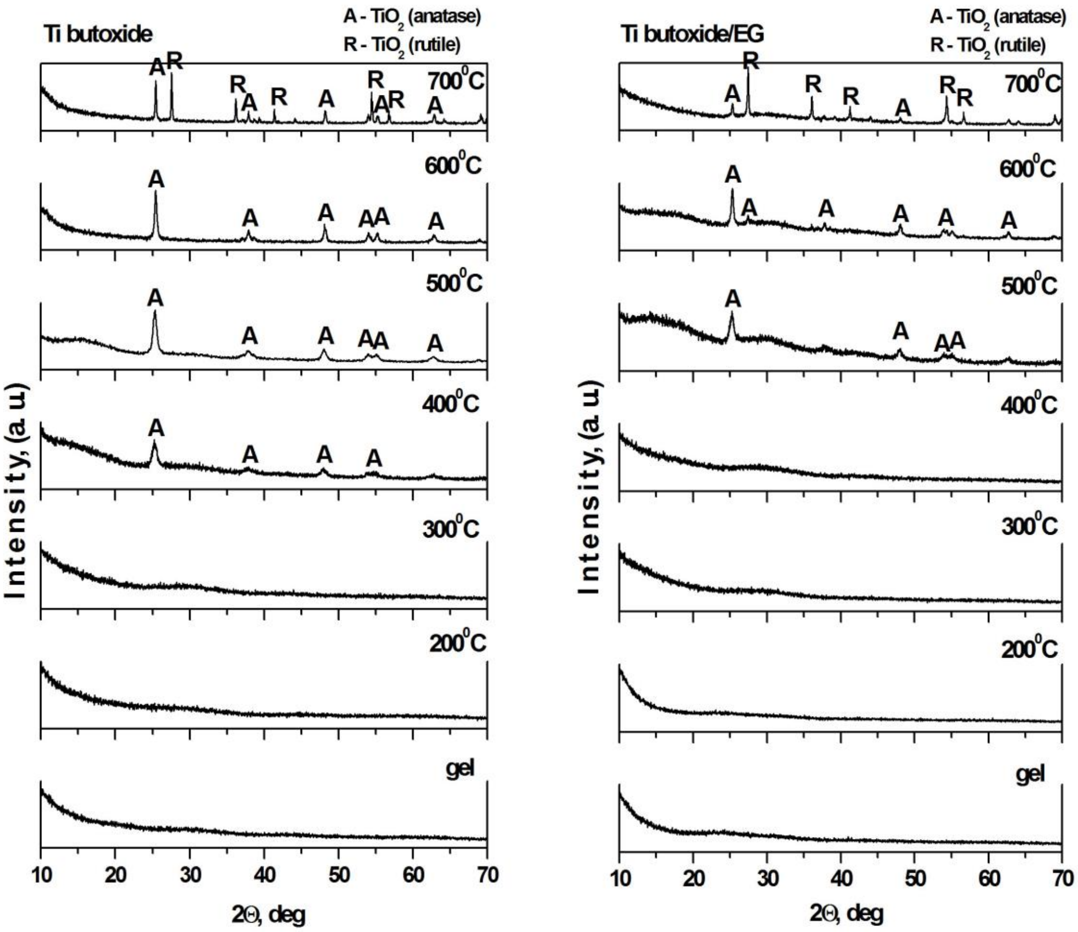

Fig. 1. XRD patterns of Ti (IV) n-butoxide (TBT) and Ti (IV) n-butoxid dissolved in EG (1:1) (TBT/EG) at different temperatures: (A) TiO_2-anatase, (R) TiO_2-rutile**)**.

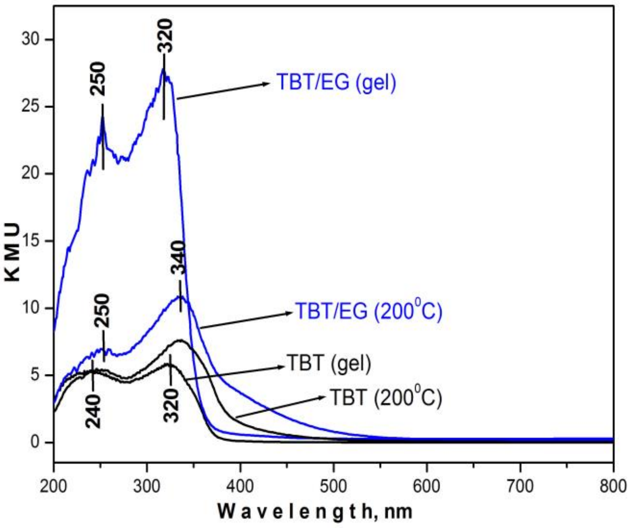

Fig. 2. UV-Vis spectra of TBT and TBT/EG: gels and heat treated at 200 °C.

IR spectroscopy

The IR spectroscopy is used for monitoring the rate and degree of hydrolysis and condensation process as well as the phase transformations in the gels during the heat treatment (in the temperature range 200-500 °C). The obtained by us IR spectra of TBT and TBT/EG are shown in Fig. 3a,b. The assignments of the vibrational bands of separate structural units are made on the basis of well-known spectral data for the precursors (Ti(IV) n-butoxide), etylen glycol (solvent), n-butanol (product of the hydrolysis-condensation reaction), crystalline TiO_2 (anatase) and TiO_2 (rutile). According to the literature data [23-25] pure Ti(IV) n-butoxide precursor is characterized by bands located between 1500-1300 cm^{-1} assigned to the bending vibrations of CH_3 and CH_2 groups. The band at 1130 cm^{-1} is characteristic for the stretching vibrations of Ti-O-C, while those at 1100 and 1040 cm^{-1} are assigned to the vibrations of terminal and bridging C-O bonds in butoxy ligands. Broad absorption bands below 1000 cm^{-1} correspond to C-H, C-O and deformation Ti-O-C vibrations [23, 26]. The ethylene glycol possesses asymmetric and symmetric stretching vibrations of C-O bonds in CH_2-OH groups at 1090 and 1040 cm^{-1} while in the spectrum of butanol they appeared at 1110, 1050 cm^{-1} along with a very intensive band at 1070 cm^{-1} [27,28]. The IR spectrum of TiO_2 (anatase) is characterized by bands at 620 - 610 and 480 - 470 cm^{-1} [29,30] connected with the vibrations of TiO_6 units. As supporting information, the measured by us spectra of ethylene glycol and 1-butanol, are presented in Fig. 4.

Obviously, the absorption region 1100 - 1020 cm^{-1} is very complex due to the overlapping of the vibrations of different structural units from Ti(IV) butoxide, EG and n-butanol. Irrespective of the existing spectral restrictions several authors [23, 24] use these bands for the interpretation of hydrolysis-condensation processes. Looking at the IR spectra of obtained by us TBT and TBT/EG gels (25 °C) (Fig. 3a,b) a difference could be seen regarding the intensity of a band centered at 1130-1120 cm^{-1}. In the TBT spectrum this band is well defined at 1130 cm^{-1}, due to the uncompleted hydrolysis reaction. In the TBT/EG spectrum it is transformed into a shoulder and shifted to 1120 cm^{-1} may be as a result of breaking of the Ti-O-C linkage. Another important band is that at 1100 cm^{-1} in TBT which is shifted to 1080 cm^{-1} in TBT/EG and its intensity increases as a result of the separation of butanol due to the greater degree of hydrolysis-condensation reactions. Additional confirmation for this suggestion is the decrease of bands intensity in the range 640 - 610 cm^{-1} (Fig. 4) which is a characteristic feature of n-butanol. There is also a broad band in the IR spectrum of TBT at 790 cm^{-1} that could be connected to the vibrations of butoxy groups. But this band is negligible in the spectrum of TBT/EG.

Heating of the gels up to 250 °C (Fig. 3) led to a strong decreasing of the bands in the range 1500 - 1300 cm^{-1} that are typical for the vibrations of CH_2 and CH_3 groups. A decrease in the bands intensity at 1120, 1080 and 1040 cm^{-1} as a consequence of decreasing of the number of non-hydrolyzed butoxy groups is also observed (Fig. 3). The spectra above 300 °C showed two strong bands near 620 and 480 cm^{-1} that are typical for the vibrations of TiO_6 building units (Fig. 3) [27,28].

It has to be mentioned that at 500 ^{o}C the IR spectra of both samples exhibited bands in the

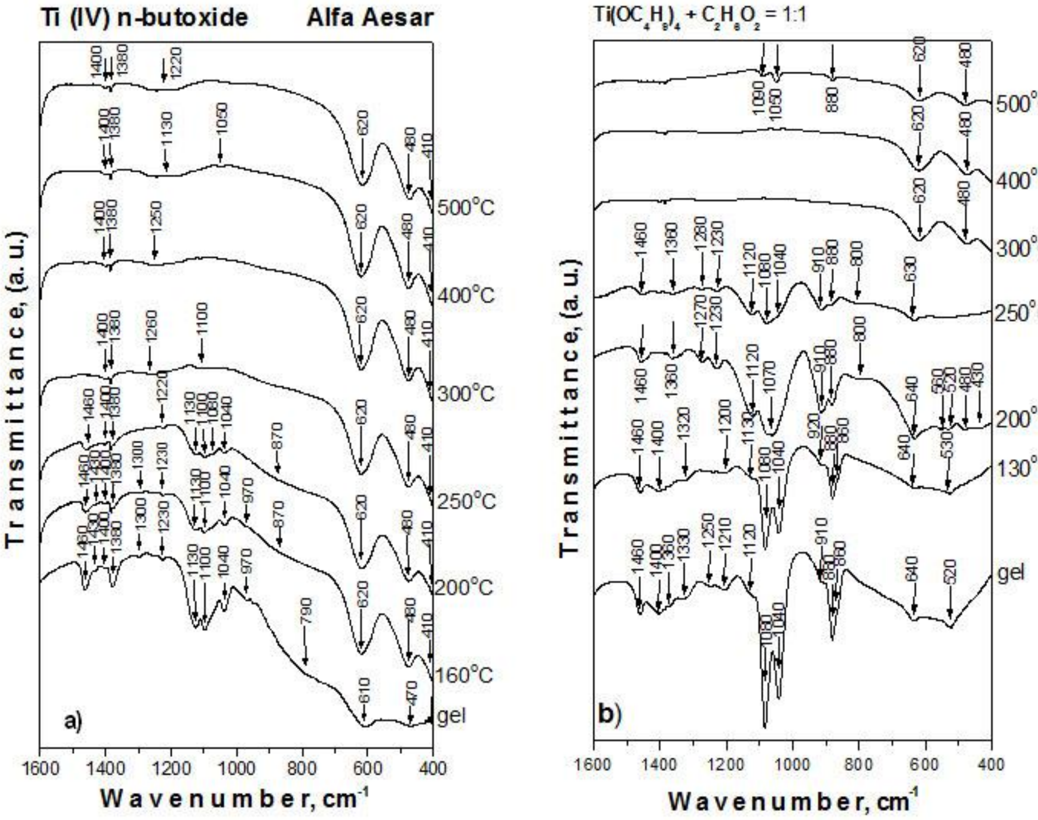

Fig. 3. IR spectra of TBT and TBT/EG: gels and heat treated up to 500 °C.

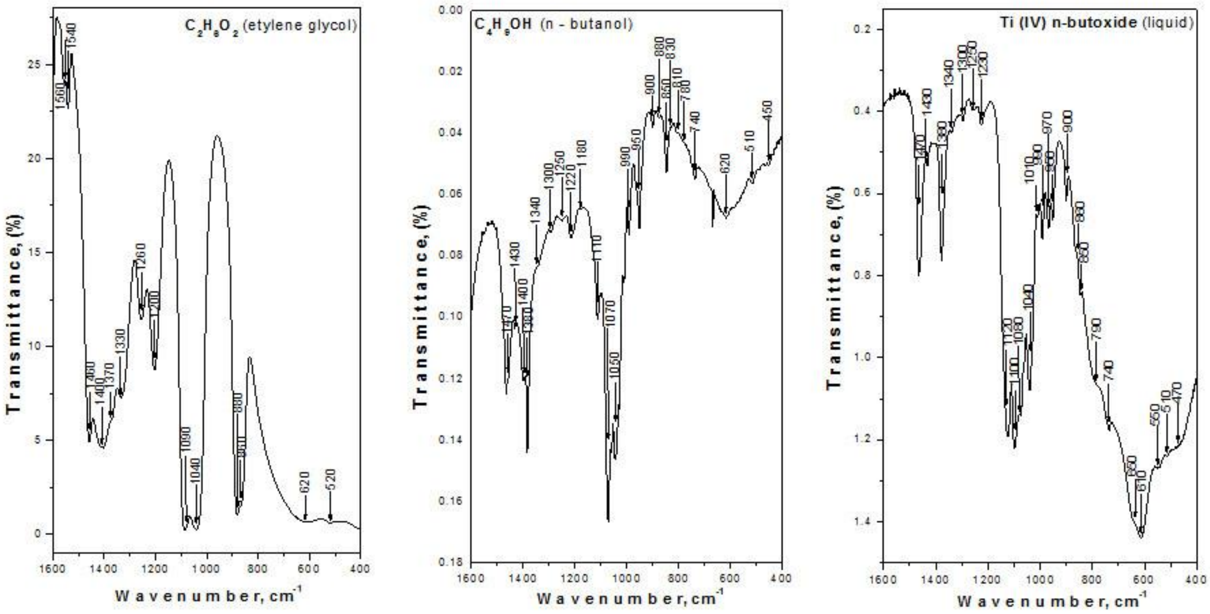

Fig. 4. IR spectra of the used precursors: a) EG, b) n-butanol and c) Ti (IV) n-butoxide.

ranges 1400 - 1220 cm^{-1} and 1090 - 1050 cm^{-1} that could be related to the presence of residual carbon, participating in different organic groups. In our previous investigations [20, 21], by DTA analysis it was established that the carbon exist in the samples even above 500 ^{o}C

Analysis of the results

Generally, in our experiments we did not introduce water in order to prevent the non – equilibrium fast hydrolysis of Ti butoxide as well as to avoid obtaining of inhomogeneous gels. Transparent, homogeneous and monolithic TBT and TBT/EG gels have been prepared at presence only of air moisture. From the obtained results is seen that the hydrolysis-condensation processes in both cases are not completed at room temperature and continue in a wide temperature range along with the decomposition of the organic groups. The discussion on the completeness of hydrolysis-condensation processes and transformation of the amorphous gels into nano-crystalline TiO_2 powders is made bearing in mind the changes in the intensity along with shifting of the IR bands (1120, 1080 and 1020 cm^{-1}) as well as the UV-Vis bands (250 and 320 nm). The strong IR band at 1080 cm^{-1} (due to separation of n-butanol) in the TBT/EG indicates fuller hydrolysis. The stronger intensity of UV – Vis band about 320-340 nm as compared to 240-250 nm is a proof for transformation of TiO_4 to TiO_6 units. This is observed in the UV-Vis spectra of TBT/EG gel and heated at 200 °C sample, which suggest a higher degree of polymerization processes. Obviously, in presence of EG a higher degree of hydrolysis - condensation reactions is achieved.

CONCLUSION

Two homogeneous titania gels obtained with and without addition of EG in presence only of air moisture are prepared. It was established that etlylene glycol preserved the mixed organic–inorganic amorphous structure at higher temperature (400 °C). The spectral analyses revealed a completeness of hydrolysis – condensation reactions in the TBT/EG in comparison to pure TBT gel. A more completed conversion of TiO_2 (anatase) to rutile is registered at 700 °C in the TBT/EG sample.

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ВЛИЯНИЕ НА ЕТИЛЕН ГЛИКОЛА ВЪРХУ ХИДРОЛИЗНО – КОНДЕНЗАЦИОННОТО ПОВЕДЕНИЕ НА Ti(IV) БУТОКСИД

Ст. И. Йорданов[1], А. Д. Бъчварова – Неделчева[2*], Р. С. Йорданова[2]

[1] *Институт по металознание, съоръжения и технологии с Център по хидро- и аеродинамика „Акад. Ангел Балевски“ - БАН, ул. "Шипчеснки проход" 67, 1574 София, България*

[2] *Институт по Обща и Неорганична Химия - БАН, ул. “Акад. Г. Бончев”, бл. 11, 1113 София, България*

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(Резюме)

Целта на изследването е да се провери влиянието на етилен гликола (ЕГ) върху скоростта на протичане на хидролизно – кондензационните процеси при получаването на гели от титанов бутоксид. Два хомогенни гела са получени със и без добавяне на етилен гликол в присъствие само на атмосферна влага. Чрез РФА бе установено, че гелът (ТБТ), получен от титановият бутоксид без добавяне на ЕГ е аморфен до 300°C, докато този получен от титановия бутоксид разтворен в етилен гликол (ТБТ/ЕГ) е аморфен до 400 °C. Доказано бе, че доминиращата кристална фаза при нагряване до 600 °C е TiO_2 (анатаз) а при 700 °C е регистриран и TiO_2 (рутил). Спектралните анализи (ИЧ и УВ – Вис) установиха протичането в по-пълна степен на хидролизно – кондензационните реакции при TBT/EG в сравнение с чистия TBT. УВ - Вис спектрите на гела съдържащ ЕГ показаха едно отместване на абсорбционния ръб към по-високите стойности на дължината на вълната (“red shifting”) в сравнение с чистия ТБТ гелантиоксидантна активност.